FINAL REPORT

Rational Selection of Tailored Amendment Mixtures and Composites for In Situ Remediation of Contaminated Sediments

SERDP Project ER-1491

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Rational Selection of Tailored Amendment Mixtures and Composites for In Situ Remediation of Contaminated Sediments

SERDP Project # ER 1491

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Acronym List

AC	activated carbon
AET	apparent effect threshold
APG	Aberdeen Proving Grounds
ASTM	American Society for Testing of Materials
ATC	engineered titanosilicante adsorbent
ATS	activated carbon embedded with ATC
BAF	bioaccumulation factor
COC	contaminants of concern
DDT	deflagration-to-detonation transition
DoD	Department of Defense
ERDC	The Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
GAC	granular activated carbon
HGR	sulfur impregnated activated carbon
MCA	Menzie Cura and Associates
MRM	Minimum Required Migration Distances
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PI	Principle Investigator
PIMS	phosphate induced metals stabilization
QA/QC	Quality Assurance/quality control
R&H	Rohm and Haas Company
SBIR	Small Business Innovative Research
SERDP	Strategic Environmental Research and Development Program
Th-SAMMS	thiol-amended mesoporous silica
TIE	toxicity identification evaluation
UMBC	University of Maryland , Baltimore County
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency

I. EXECUTIVE SUMMARY

Emerging laboratory-scale research by our group and others has shown that contaminant transport pathways and bioavailability can be interrupted in-situ by modifying and enhancing the contaminant assimilation capacity of natural sediments. This is achieved by adding amendments such as activated carbon for binding persistent organic pollutants and natural minerals such as apatites, zeolites, or bauxite for the binding of toxic metals in sediments. This research was focused on advancing in-situ remediation of contaminated sediments by comparing different sorbents, either alone or in formulated combinations of new amendments, improving scientific understanding of how multiple amendments function together and reduce contaminant bioavailability, and developing efficient delivery methods for applying amendments to impacted sediments.

Results presented in this report indicate that with suitable combination of sorbents, sorption of metals and organics can take place simultaneously. A primary list of 75 potential sediment amendments were identified from those currently under development for remediation of individual sediment contaminants and from existing industrial sorbents used for water- and gas-phase treatments. Initial screening was based on literature information on sorptive/degradative capacity, potential ecological effects in the sediment environment, and potential complications during deployment such as material density, erodability, decay or transformation in freshwater and saltwater environments. The screening produced a list of eleven sorbents that were used for further sorption testing of metals and organics.

Based on pH-edge sorption tests, natural sorbents were eliminated due to inferior performance. The potential as in-situ sediment amendment was explored by comparing the sorption properties of the engineered amendments in freshwater and saltwater matrices. Thiol-amended mesoporous silica (Th-SAMMS) and a titanosilicate mineral (ATS) demonstrated the highest sorption capacity for Cd and Pb respectively. Sequential extraction tests conducted after mixing engineered sorbents with contaminated sediment demonstrate transfer of metal contaminants from a weakly bound state to a more strongly bound state. Biouptake of Cd and Pb into freshwater oligochaetes was evaluated after the sediment was amended with Th-SAMMS and ATS, respectively. Biouptake of Cd was reduced by 98% after amendment of Thiol-SAMMS. The speciation of Cd was also altered with large reductions in the easily extractable fractions. However, the reduction of biouptake of native Pb was insignificant while the treatment reduced easily extractable portion of Pb in the sediment.

Th-SAMMS demonstrated the highest sorption capacity for Hg in both freshwater and saltwater matrices. Treatment of Peninsula Harbor freshwater sediment with sorbent amendments resulted in lower MeHg bioaccumulation factors in benthic organisms ($P < 0.05$). The treatments reduced MeHg worm BAF by 54 % (GAC), 58% (HGR), and 83% (Thiol-SAMMS). Biouptake reduction of Hg and methylmercury was achieved for both artificially spiked and native mercury present in sediments. Thiol-SAMMS added to sediment along with activated carbon reduced bioaccumulation of native Hg, Me-Hg, and PCB present simultaneously in sediments. With the individual and mixture placement of the amendments, the reductions were more than 90 % for MeHg, which indicated the reductions were not as sensitive to co-existence of the amendments.

Most amendments were nontoxic in chronic exposures. Organism survival in sediment amended with ATC, ATS, ConSepC, and HGR were not statistically different from the control for all

endpoints evaluated. The toxicity observed for Thiol-SAMMS was moderate at a dose of 5% by dry weight with a reduction in *H. Azteca* survival from 98% to 73%. Although Thiol-SAMMS reduced survival in clean control sediments, it may increase survival of organisms in mercury contaminated sediments to levels that may be acceptable for meeting remediation goals. For example, *L. plumulosus* survival in diluted Augusta Bay sediment was 24% compared to a survival of 69% in the same sediment after amendment with Th-SAMMS.

Sorbent agglomerates were developed with the following properties: dense enough to sink through the water column and provide a light non-suffocating layer on the sediment, dense enough to be resistant to resuspension over the period it takes to be worked into the sediments, and able to break down to release active agents over the period of days to weeks. In addition, the binders used for the agglomerate were non-toxic. The most promising formulation was made of powdered activated carbon, clay, and sand and was produced in larger quantities for use in biological tests. In biouptake experiments, the carbon incorporated as a pellet was as effective in reducing the bioaccumulation of PCB as powdered activated carbon applied directly, indicating that the pellets can break down and be mixed effectively into the active layer by bioturbation.

Technology transition efforts were significantly boosted through additional funding from an USUSEPA Small Business Innovative Research (SBIR) project and partnership with a small business (Menzie Cura and Associates [MCA]; Dr. C. A. Menzie). The partnership resulted in the development of an amendment delivery platform in the form of engineered pellets named "SediMite™". Development of the agglomerate involved testing a variety of materials for the ability to form the agglomerate using scalable laboratory techniques, testing the physical characteristics of the resulting agglomerates, and testing the interaction of the activated carbon and other agglomerate additives. The most promising formulation was made of powdered activated carbon, bentonite clay, and sand. Through this effort, the product manufacture was scaled up at a large-scale production facility using high throughput equipment capable of production rates of 3.5 million pounds per year.

Two recently funded technology demonstration projects are evaluating the effectiveness of amendment pellets "SediMite™" in the field through ESTCP funding (ER-0835 and ER-0825). Several partnerships were developed with private industry (Rohm and Haas, DuPont, and Dow Chemical) and DoD sites (Ft. Eustis, and Aberdeen Proving Ground) to take the technology forward into pilot-scale demonstrations. Based on discussions with site managers and regulatory agencies, the following scenarios represent the most viable commercial applications of this technology:

- Application to sediments that pose low to moderate risk where alternatives other than dredging would be desirable;
- Applications to sensitive environments where it is desirable to minimize habitat disruption (these include contaminated sediments located in aquatic or marine grass beds and wetland environments);
- Application to hard to reach places (e.g., in and around pier structures)

It is anticipated that the technology developed through this project will be transitioned to full scale remedial applications through recently started and future pilot-scale studies.

II. OBJECTIVES

The overall objective of this research was to develop sorbent mixtures and composites that can stabilize combinations of organic and metal contaminants in sediments. We presented the following key hypotheses in the research proposal:

1. Multifunctional amendments may be used to address organic and inorganic contaminant mixtures in sediments by uniquely targeting the chemical properties of each contaminant type. Multifunctional amendments used for other purposes already exist in industry. Therefore, the ability to manufacture such amendments is well established. We hypothesized that existing amendments may be suitable for sediment remediation, or that new composites can be designed and manufactured to address complex contaminant mixtures in sediments.
2. To date, there is little information on the functional overlap and redundancy of various individual amendments, and there is no rational framework for comparing amendment efficiencies and selecting functional amendments for in situ sediment remediation. We hypothesized that addressing these key issues will provide powerful support for site-specific management decision-making processes when selecting and designing remedial alternatives for contaminated sediment sites.
3. In addition to offering unique sorptive/reactive properties to control contaminant bioavailability, multifunctional amendment composites may be designed to facilitate placement of amendments in sediments. We hypothesized that composites can readily be designed to increase the specific gravity, settle ability, and stability of surface sediment amendments, to facilitate deployment and surface-sediment contact.

To test these hypotheses, we proposed a rational approach for tailoring amendments that can reduce the bioavailability of multiple contaminants of concern and to test the efficacy of those amendments in the laboratory. The selected multifunctional additives were tested for reduction of contaminant bioaccumulation using field sediments. The following four specific research objectives were designed to test and validate the above hypotheses:

1. Develop a rational selection process for multifunctional amendments based on established and emerging knowledge in the field of in situ sediment remediation
2. Evaluate interactive relationships among selected sorbent amendment materials
3. Adapt traditional material science techniques to create multifunctional amendment mixtures and composites that have the necessary physical stability, sorptive/destructive properties, and mass transfer properties to address complex contaminant mixtures in sediments
4. Evaluate the effectiveness of amendment mixtures/composites on sediments from DoD sites containing complex mixtures of organics, metals, and metalloids.

III. PROJECT BACKGROUND

Challenges in Sediment remediation. In aquatic environments that are impacted by contaminated sediments, risk management strategies focus on interrupting potential exposure pathways by which contaminants might pose an ecological or human health risk over time. Conventional approaches achieve this goal by isolating contaminated sediments (capping), or removing contaminated sediments from the environment (dredging)(1, 2). However, both dredging and conventional capping have severe limitations such as the need for large-scale material handling. In the case of dredging, these materials can be highly contaminated and require off-site transport. Dredging and capping are costly and tend to be largely destructive of the native benthic environment. Dredging often has difficulty achieving risk reduction goals (i.e., low sediment contaminant concentrations) due to sediment suspension and redeposition during dredging. Off-site placement also tends to be problematic both because of the large-scale sediment handling requirements, and because the contaminated media is simply relocated, and contaminants are neither destroyed nor permanently sequestered.

In-situ techniques are needed that are less energy-intensive, less expensive, and less disruptive of the environment than conventional technologies, can reduce ecosystem exposure, and are defensible through well grounded scientific understanding of contaminant transport behavior in field conditions. It is known that the binding of contaminants into organic or inorganic sediment matrices, reduces porewater contaminant concentrations and reduces contaminant bioavailability (3-5). The contaminant sorption capacity of natural sediments may be modified and enhanced by the addition of such amendments as activated carbon for persistent organic pollutants; natural minerals such as apatite, zeolites, or bauxite and refined minerals such as alumina/activated alumina for metals or metalloids; ion exchange resins for metals or other inorganic contaminants; zero-valent iron (microscale or nanoscale) for PCB dechlorination; or lime for pH control or nitroaromatics degradation.

Binding and availability of organic contaminants. Recent work by Ghosh (the Principle Investigator [PI] of this proposal) and others proposes that hydrophobic organic contaminants in sediment may be of more or less concern depending on how weakly or strongly they are sorbed to sediment organic matter (6, 7). In recent award-winning SERDP-funded work, Ghosh and collaborators demonstrated that PCB and PAH in the sediment tended to preferentially accumulate in coal-derived and char particles where the compounds were strongly bound (3) Building on these observations, they showed that addition of activated carbon sorbent to sediments reduces PCB and PAH bioavailability (8, 9).

Activated carbon also may be an effective method to manage organometals, specifically methyl-Hg. Whereas activated carbon has been shown to greatly reduce bioavailability of PCB in sediments (9), its effect on elemental and methyl-Hg bioavailability in sediments shows great promise, but is less established (10, 11). Further research is needed to understand principles of mercury rUSEPArtitioning onto sorbents and to optimize carbon types for methyl-Hg and carbon amendments for inorganic Hg sequestration and control.

Binding and availability of metal contaminants. The availability of inorganic metals in sediments is controlled by the surface chemistry of geosorbents and precipitation (5, 12). Sorption and

precipitation are important chemical processes that regulate the solubility and partitioning of metals between solution and solid phases in sediments, and metal bioavailability to exposed organisms. In anaerobic sediments, metals are strongly bound to reversible sulfide complexes; under aerobic conditions metals partition onto organic carbon matrices, iron and manganese hydroxides, or onto mineral surfaces (13). Metal cations also form sparingly soluble phosphates, carbonates, sulfides, and hydroxides that can be exploited to stabilize contaminated sediments. Natural minerals such as apatite, zeolites, or bauxite and refined minerals such as alumina/activated alumina have been tested for sequestration of metals or metalloids (14-18); ion exchange resins have been tested for metals or other inorganic contaminants (19); and lime has been proposed for pH control (20) or nitroaromatics degradation (21). For example, the recently demonstrated Phosphate Induced Metals Stabilization (PIMS) technology uses apatite for stabilizing lead in contaminated soil (22). However these metal-binding additives have not been examined in sediment matrices where organic co-contaminants also may be present as major drivers for human health and ecosystem risk.

These exciting findings in the sorption and bioavailability of metal or organic contaminants in sediments need to be synthesized into a rational framework before these technologies can be applied to the majority of impacted sediment sites where multiple contaminants exist. An important need in the field of in situ sediment remediation, as emphasized by the SERDP/ESTCP expert panel workshop, is the development of new amendments and an improved scientific understanding of modes of action. We believe that the greatest challenge lies in being able to develop a rational framework to compare and contrast different sorbents, either alone or in formulated combinations, to achieve in situ clean up goals for multiple contaminants of concern at a given site.

<u>Multifunctional Sorbents.</u> Identification and selection of the appropriate amendment or amendment mixtures (i.e., multifunctional amendments) depends upon the efficacy of the various amendments to reduce the bioavailability of site specific contaminants, functional interactions of multiple amendments in mixtures, and biological effects of the amendments in the natural environment. If properly selected, multifunctional amendments could address complex contaminant mixtures in sediments, and subsequently could be engineered to facilitate placement in aquatic environments. Multifunctional amendments already exist as industrial catalysts or sorbents for aqueous or gas phase applications, where activated carbon serves as the backbone (for hydrophobic partitioning) and either is impregnated with the target amendment or blended in a briquette-like composite using an appropriate and non-toxic binder (23-27).

Activated carbons offer a promising foundation for multifunctional sorbent composites, due to their heterogeneous sorptive properties not only for organic contaminants, but also for metals (28). Reed (29) reported on the metal removal ability of numerous commercially available activated carbons. Metal removal differed widely between carbons and metal types; however, for all carbon-metal combinations, removal was a strong function of pH. For cationic metals, removal increased with pH, and for metal anions the opposite behavior was observed. Thus, if activated carbons are to be used in a remediation setting for metals the effect of pH must be accounted for. Activated carbons can also be impregnated by various salts, elements, and oxides to attribute unique sorption properties. For example, activated carbon impregnated with sulfur is a mature technology that has been used effectively for mercury removal from flue gases and

water (25, 30). Reed impregnated an activated carbon with Fe(III) oxides and investigated the removal of several anionic and cationic metals (23, 27). Metal removal increased significantly over that observed for the virgin carbon and also was a strong function of pH. Impregnation of the carbon decreased the surface area (21%), total pore volume (23%) and iodine number (20%).

Activated carbon can also be impregnated by commercially available ion exchange materials. Cd(II), Pb(II) and Zn(II) were effectively removed by these types of impregnated carbons (24), but the effect on organic adsorbate removal requires additional study. Despite the promise of these results, questions remain regarding how effectively the impregnated carbons will reduce the bioavailability of metals and organics simultaneously in sediments; the role of pH in metals sequestration using novel carbon amendments, particularly in natural environments; whether sorption of organic contaminants is affected by the impregnation processes; and whether various organic and/or inorganic compounds compete for sorption sites.

IV. MATERIALS AND METHODS

i) pH adsorption edge experiments. Appropriate weights of $NaNO_3$ salt were added to deionized water to achieve an ionic strength of 0.01 M as $NaNO_3$. Solution was stirred to dissolve salts prior to addition of a volume of stock solution (10 g/L) of the heavy metal being tested (Cd or Pb) to bring final metal concentration to 100 parts per billion (ppb). The adsorbent being tested was then added by mass (preliminary experiments tested all materials at 100 mg/L) to this solution as it stirred. From this stirring mixture, 40 ml aliquots were withdrawn using a wide mouth pipette and delivered to 50 ml plastic bottles. The first bottle in the series was titrated by hand with 0.1 N HNO_3 to a pH of 3. The final bottle in the series was titrated by hand with 0.1 N NaOH to a pH of 10. The remaining bottles in the series were then titrated using either 0.1 N HNO_3 or 0.1 N NaOH to pH values of between 3 and 10. All bottles in series were then capped and put on the tumbler for 48 hours. Upon removal from the tumbler, samples were read for pH, filtered using 0.45 µm membrane filters, and preserved using concentrated nitric acid. Samples were then analyzed for heavy metal using a graphite furnace atomic absorption spectrometer.

ii) Iodine Number Test. Iodine tests have been regarded as an industry wide standard for measuring a materials' sorption capacity. The iodine number of a material, which is the amount of iodine absorbed per gram of material used, is a relative indicator of porosity and an approximation of surface area. This set of experiments provided a simple process for acquiring accurate data that can be used to compare and select materials for further testing. The ASTM standard test method (D 4607) for determination of iodine number was followed. The materials tested were granular activated carbon (GAC), alumina powder, ATS, apatite, bentonite, barite, ConSep 20 and 42%, and ATC.

iii) PCB/PAH Isotherm Tests Using Polyoxymethylene Solid Phase Extraction. Measuring low aqueous concentrations of PCB and PAH at nanograms per liter levels is challenging especially for laboratory adsorption experiments using strong sorbents and where large volumes of water may not be available. A relatively novel technique using polyoxymethylene solid-phase extraction (POM-SPE) has been used successfully to measure PAH sorption isotherms in coals and black carbon (31) and was used for this study. In this method the sorbent is equilibrated with water and different amounts of sorbate in vials containing POM strips. The hydrophobic contaminants adsorbed on the POM strips are extracted and measured providing an estimate of the low aqueous concentrations based on independently measured sorption isotherms for the POM strips. This method provides a number of advantages over conventional batch test methods, including easy USEPA ration of fine particles and enhancing detection limits.

All POM calibration experiments were carried out in 250 or 40 ml glass vials. The mass of POM strips was about 20 mg for each reaction vials. Vials were filled with a synthetic ground water (100 mg/L sodium azide and 0.01 M calcium chloride). POM strips were then added and the systems spiked with known amount of PCB or PAH. For example, Table 1 shows the amount of PCB spiked for the PCB-POM calibration experiment.

Table 1. Total PCB amount injected in each Isotherm set (ug)

congener	1	2	3	4	5	6
9	35.48	15.4849	1.1248	0.246	0.01289	0.001465
18	23.025	16.8537	1.2872	0.284	0.01479	0.001655
47	0.925	0.9445	0.8944	0.193	0.01017	0.001185
101	0	0.0647	0.5144	0.643	0.03331	0.003715

All equilibration vials were horizontally shaken at room temperature for 35 days. The POM was then removed and the organics were extracted by pure hexane using a series extraction method over a 3 day period. The dissolved organics were also extracted by adding hexane to each reaction vial. The systems were agitated vigorously for about 3 minutes (three times) and the supernatant (hexane) were transferred to a clean vial for further processing. The calibration was set up using four PCB and 16 PAH compounds. There are six levels of initial spiking concentration and within each set at least three replicates and two blank solutions were prUSEPAred for each concentration. Analyte measurements were performed by GC/MS for PAH and GC/ECD for PCB.

iv) Analytical Method for PCB. Soil/tissue PCB were extracted following USEPA method 3550B using three volumes of 40 mL each of acetone-hexane mixture (1:1) and sonicating the slurry for 6 minutes (pulsing for half minute on and half minute off). Pesticide grade hexane and acetone were used for all extractions. USEPA method 3630C was followed for sample cleanup where, the dried and concentrated extract was passed through a deactivated silica gel column for the removal organic interferences. If all interfering compounds were not removed by the silica gel cleanup method, additional cleanup methods 3665A (sulfuric acid cleanup) and 3660B (Sulfur removal with copper) were be implemented. PCB congener specific analysis was performed using a modified USEPA SW846 Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm ID) and a micro electron capture detector were used for analysis. A 5-level PCB calibration table was prUSEPAred using a known PCB mixture containing 250 μg/L of Aroclor 1232, 180 μg/L of Aroclor 1248 and 180 μg/L of Aroclor 1262 yielding a total PCB concentration of 610 μg/L. The known PCB calibration mixture was obtained from the USEPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan. Concentrations of individual PCB congeners in the mixture were obtained from Mullin (1994)(32). Two internal standards used were: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2',3,4,4',5,6,6'-octachloro biphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, 92 PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks are calibrated as sum of congeners.

A Hewlett Packard gas chromatograph (Model 6890) with a fused silica capillary column (HP-5, 30 m x 0.25 mm I.D.) and a MS detector (Model 5973N) were used for analysis based on USEPA method 8270 for PAH. A standard mixture of 16 USEPA priority pollutant PAH compounds obtained from Ultra Scientific was used for calibration.

v) Analytical Methods for Metals. For Cd, Pb, and Zn, sediments were digested using either USEPA Method 3050B or 3051 (digestion) and then analyzed by either a Perkin Elmer 4100 Graphite Furnace Atomic Absorption Spectrophotometer using USEPA methods 7131A (Cd), 7421 (Pb), and 7951 (Zn) or induced coupled plasma mass spectrometer. For Hg, sediments were digested with HNO_3/H_2SO_4 (7:4 v/v) as described in the previous studies (33, 34). A three-tiered quality assurance/quality control procedure was adhered to in the processing of all analytical samples.

1. At least 10% of all samples were randomly collected in triplicate then analyzed as a QA/QC check on the system being studied.
2. At least 10% of all samples were randomly analyzed in triplicate as a QA/QC check on the instrument. (Thus, sufficient volume will be collected in all sampling events for potential triplicate analysis.)
3. Analytic recoveries were performed on at least 10% of all samples as a QA/QC check on the analyst.

All statistical analysis and data reduction were performed in accordance with guidelines established in USEPA QA/G-9, Guidance for Data Quality Assessment, Practical Methods for Data Analysis. As experimental data were analyzed, a formal structure to identify and account for "outliers" was established and data will be further reduced according to Section 4.4 in USEPA QA/G-9. When triplicate experiments were performed statistical comparison mechanisms prescribed in USEPA QA/G-9 were followed.

vi) Biouptake Studies for Organic and Metal Contaminants.

L. variegatus bioaccumulation studies. For the biouptake study, the USEPA test method for measuring the bioaccumulation of sediment-associated contaminants in *L. variegatus* (35) was followed. After sediment-amendment mixing, known amount of the sediment-amendment mixture was transferred to mesocosm containers. Equal volumes of spring water were added to each mesocosm and allowed to settle overnight. Forty fresh worms were introduced to each beaker. The worms were allowed contact with the sediment for known time periods before analysis. During contact, the level of overlying water was maintained and the worms were not fed. At the end of each contact period, about 40 ml of the overlying water was filtered and preserved using concentrated nitric acid for estimation of aqueous contaminant concentrations. The remaining overlying water was removed and the worms were collected by wet sieving. Overlying water quality parameters (temperature, DO, pH, general hardness and alkalinity were measured prior to sieving. The retrieved worms were allowed to depurate in spring water for 6 hrs, sUSEPArated from the depuration, weighed, placed in a 12 mL glass vial and stored in a freezer for tissue analysis. For Cd analysis, the worms were digested with concentrated analytical grade nitric acid (about 2-3 mL per 100 mg wet weight) at a temperature of 100°C (36). For Pb, the tissue was digested with a mixture of nitric acid and perchloric acid (6:1 v/v) at 100^oC (37). For Hg, sediments were digested with HNO_3/H_2SO_4 (7:4 v/v). The samples were diluted with 2% (v/v) nitric acid solution. The overlying water from each sample was collected, filtered and acidified in the end of worm-sediment contact for aqueous phase metal analysis. Analysis of aqueous metal concentration was carried out using an ICP/MS. PCB in worm tissue was extracted by hexane: acetone (1:1 vol/vol) and analyzed using methods described earlier.

28-d L. plumulosus bioaccumulation study**.** *Leptocheirus plumulosus* were obtained from in-house laboratory cultures. Animals were maintained, under static conditions, in 42 X 24 X 15 cm polyethylene tote boxes containing culture sediment (sieved < 250 µm) and were fed Tetramin® (Tetra, Blacksburg, Virginia, USA) three times weekly. The 28-d *L. plumulosus* experiment was conducted following methods under development at the ERDC. Experimental conditions for the *L. plumulosus* chronic experiments are outlined in Table 1.

An unamended or baseline sediment was included as a basis of comparison for determining the efficacy of the amendments to bind mercury. The required amount of sediment and amendment were weighed and placed in amber 1 gallon glass jar. The contents of the jar were mixed by hand then placed on a rolling mill apparatus. The sediment was slowly rolled for 28 days in the dark at room temperature to ensure a homogenous mixture. The day prior to test initiation, treatment sediments were removed from the roller mill and approximately 200 mL of each treatment sediment was added to 4 replicate 1 L beakers to obtain the required depth of 3 centimeters. A performance control treatment of clean SC sediment was also included in the study to evaluate test integrity. Beakers were placed in an environmental chamber under gentle aeration. Temperature was maintained at 23±1°C and light cycle was set at 16:8 lights: darkness.

At test initiation, 50 *L. plumulosus* (passing through a 2 mm but retained on a 1 mm sieve) were counted into a 150 mL counting chambers prior to addition to beakers. The contents of each chamber were gently rinsed into a treatment beaker (1 counting chamber/beaker). Water quality measurements (dissolved oxygen, salinity, pH and ammonia) were determined at day 0 and prior to test termination. Temperature was monitored daily. Each replicate beaker was provided 20 mg of Tetramin® (Tetra, Blacksburg, VA) on Mondays and Fridays. Daily observations of each beaker were conducted. Following 28 days of exposure, sediment of each treatment beaker was gently sieved (500 µm sieve) and surviving amphipods recovered. Survival was enumerated and animals were placed in clean water to depurate for 4 hours. Tissue from each treatment replicate was placed in a clean 25 mL centrifuge tube, biomass was recorded and tubes were placed in an ultra-low freezer at -80°C. Tissue was later sent on dry ice to the Smithsonian Environmental Research Center for methyl mercury analysis. Due to low tissue recovery in the control treatment, replicates A& B and C& D were combined to obtain enough tissue for methyl mercury analysis. As a result only two chemistry replicates were analyzed for this treatment.

28-d N. virens Bioaccumulation study**.** Nereis virens were obtained from Aquatic Research Organisms (Hampton, New Hampshire). Upon arrival worms were maintained in tote boxes at the proper salinity and temperature until testing. The 28-d *N. virens* experiment was conducted following guidance provided in “Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. - Testing Manual” (38). Experimental conditions for the *N. virens* chronic experiment are outlined in Table 1.

An unamended or baseline sediment was included as a basis of comparison for determining the efficacy of the amendments to bind mercury. The required amount of sediment and amendment were weighed and placed in amber 1 gallon glass jar. The contents of the jar were mixed by hand then placed on a rolling mill apparatus. The sediment was slowly rolled for 28 days in the dark at room temperature to ensure a homogenous mixture. The day prior to test initiation, treatment sediments were removed from the roller mill and approximately 600 mL of each treatment sediment was added to 4 replicate 2 L beakers to obtain the required depth of 5

centimeters. Performance control beakers containing clean SC sediment were also included. Beakers were placed in an environmental chamber under gentle aeration. Temperature was maintained at 20±1 °C and light cycle was set at 12:12 light: darkness.

At test initiation, 2 adult *N. virens were* gently placed directly into a treatment beaker. Water quality measurements (dissolved oxygen, salinity, pH and ammonia) were determined at day 0 and prior to test termination. Temperature was monitored daily. The experiment was static renewal with water exchanges occurring three times weekly. No food was provided during testing. Daily observations of each beaker were conducted. On day 28 sediment of each treatment beaker was gently sieved (500 µm sieve) and surviving worms recovered. Survival was enumerated and animals were manually depurated by clipping off the last few posterior segments then using a metal probe to force out fecal matter from the digestive tract. Tissue from each treatment replicate was placed in clean 50 mL centrifuge tube, biomass was recorded and tubes were placed in an ultra-low freezer at -80 °C. Tissue was later sent on dry ice to the Smithsonian Environmental Research Center for total and methyl mercury analyses.

<u>vii) Metal Sequential Extraction</u>. Sequential extractions for Cd and Pb were carried out following a modified procedure performed by Tessier et al. and Terzano et al. (39, 40), which involved five steps: i) <u>Exchangeable fraction</u>: extraction at room temperature for 2 hr with 1M of ammonium acetate with pH adjusted to 7. The system was agitated continuously on a shaker. ii) <u>Acid-soluble fraction</u>: extraction at room temperature for 2 hr with 1 M of ammonium acetate with pH adjusted to 5 with nitric acid. iii) <u>Reducible fraction</u>: extraction at 95 ± 7^{o}C for 6 hr with 0.04 M of hydroxylamine hydrochloride in 25% acetic acid. iv) <u>Oxidizable fraction</u>: extraction at 85 ± 5^{o}C for 2 hr with 30 % hydrogen peroxide. v) <u>Residual fraction</u>: reflux with aqua regia solution (1:3 volume ratio of nitric acid and hydrochloric acid) for 2 hr. Mercury separation into fraction involves the following four steps: i) water soluble: extraction. ii) ion exchangeable Hg was extracted under pH 5 acidic condition with 1M $CaCl_2$. iii) Organic fraction was sUSEPArated by successive extractions using 0.2 M NaOH and 4% CH_3COOH (v/v). iv) Residual Hg was obtained using acid digestion described above. The extractions for proceeding three step were carried out at room temperature for 2 hr. At the end of each step for all metal sequential extraction, the sediment slurry was filtered with a 0.22 µm filter. The extract was acidified and stored for measurement.

<u>viii) Chronic Toxicity Test.</u> The required amount of clean sediment and amendment were weighed and placed in amber 1 gallon glass jar. The contents of the jar were mixed by hand then placed on a roller. The sediment was slowly rolled for 28 days in the dark at room temperature to ensure a homogenous mixture. Four different organisms were used, *Neanthes arenaceodentata*, *Chironomus dilutus, Hyalella Azteca* and *Leptocheirus plumulosus.* Tests were conducted as described in existing chronic sediment toxicity test methods (Bridges et Farrar, 1997; USUSEPA 2000; USUSEPA 2001). A known volume (75 – 175 ml, depending on the organism) of each treated sediment was added to 5-10 replicate beakers to obtain the required depth of at least 2 centimeters. Beakers were placed in an exposure module under gentle aeration. Temperature and light cycle were maintained at organism specific values. At test initiation, the appropriate number of organisms was added to each exposure chamber. Water quality measurements were measured at day 0 and prior to test termination. Temperature was monitored daily. At test termination sediment was passed through a sieve and surviving

organisms collected and enumerated. Surviving organisms were dried then weighed to determine final biomass. Reproduction was measured in the *L. plumulosus* study only.

Table 2. Experimental conditions for the *Leptocheirus plumulosus* and *Neries virens* 28-d bioaccumulation studies.

	Organism	
Parameter	***Leptocheirus plumulosus***	***Neries virens***
Amendment Addition	1 month prior to test initiation	1 month prior to test initiation
Test duration	28 days	28 days
Temperature	23±1 °C	20±1 °C
Light Quality	Wide-spectrum fluorescent lights (100 to 1000 lux)	Wide–spectrum fluorescent lights (100 to 1000 lux)
Photoperiod	16:8 Light:Darkness	12:12 Light:Darkness
Test Chamber	1 L beaker	2 L beaker
Overlying water	Artificial seawater	Artificial Seawater
Overlying Water Volume	700 mL	1400 mL
Renewal of Overlying Water	None	None
Age/Size of Organism	> 1mm and < 2mm	Adult
Number of Organisms per Beaker	50	2
Number of Replicate Beakers/Treatment	4	4
Feeding	None	None
Aeration	1 bubble/sec	1 bubble/sec
Overlying Water Quality Measurements	pH, dissolved oxygen, salinity, temperature and ammonia at the beginning and end of the test for each beaker. Temperature daily.	pH, dissolved oxygen, salinity, temperature and ammonia at the beginning and end of the test for each beaker. Temperature daily.
Endpoints	Methyl mercury tissue concentration	Total and methyl mercury tissue concentration
Test acceptability	Adequate tissue mass for detection of methyl mercury.	Adequate tissue mass for detection of total and methyl mercury.

V. RESULTS AND ACCOMPLISHMENTS

There were five major tasks that were proposed and accomplished in this research: 1) the first task involved identifying and screening potential amendments and mixtures based on a theoretical understanding of various amendments, based on past work conducted by this research team, and on literature reports by others. The most promising sorbent mixtures were carried forward into the next task. 2) The second task involved aqueous phase removal tests and isotherm measurements for selected organic and metal contaminants to further decide on the most promising sorbents. 3) The third task evaluated effects of interaction among different amendments. In particular the experiments evaluated changes in sorption capacity of activated carbon in the presence of metal adsorbents. 4) The fourth task adapted traditional material science techniques to create amendment mixtures and composites that have the necessary physical stability, sorptive properties, and mass transfer properties for application to sediment environments. 5) The fifth task involved testing of toxicity of the selected amendments and effectiveness of the amendments in reducing contaminant bioavailability in sediments.

Milestones 3 and 4 that involved formulation of amendment mixtures into composite materials was enhanced in scope and advanced ahead of schedule. This was made possible through additional leveraged funding from an USEPA Small Business Innovative Research support (awarded to C.A. Menzie) and collaboration with an environmental consulting company (Menzie Cura and Associates). The enhanced scope included detailed testing of formulated pellets in the laboratory, evaluation of commercialization potential, and trial large scale production in an industrial unit.

Accomplishments from the five tasks have been written as research papers for submission to journals for publication. Three journal publications are anticipated from the research outcome of this project and are listed below:

Tasks 1 and 2: paper titled: "*Evaluation of sorbent amendments for in situ remediation of metal contaminated sediments*".

Tasks 3 and 4: Paper titled: "*Development and testing of a low-impact delivery system for sediment amendments*"

Task 5: Toxicity and bioaccumulation studies, paper titled: "*Bioavailability reduction of PCB and mercury in sediments using multifunctional amendments*"

The five accomplished tasks are described briefly below. Draft papers listed above present the detailed results and interpretations and are presented in the Appendix.

Task 1: Select potential amendments. Task 1 involved identifying and screening potential amendments and mixtures based on a theoretical understanding of various amendments, past work conducted by this research team, and literature reports by others. A literature review was conducted to glean as much information as possible on sorptive materials developed in various fields of science and engineering. Special focus was in the fields of water treatment, air and exhaust gas treatment, industrial catalysts and adsorbents, ion exchange resins and zeolites. The collected information on the different types of sorbents was categorized based on target contaminants and modes of action. A primary list of 75 potential sediment amendments was identified from those currently under development for remediation of individual sediment contaminants, and from existing industrial sorbents used for other matrices such as water and

gas-phase treatments. The initial list of 75 potential additives having different modes of action is provided in Appendix I. The initial screening was based on literature information on sorptive/degradative capacity, potential ecological effects in the sediment environment, material density, erodability, and decay or transformation in freshwater and saltwater environments. The result of this task was the down-selection of a matrix of potential sorbents that was carried forward into Task 2. A list of sorbents selected for organic and metal sorption capacity testing is provided in Table 3. This list includes single sorbents as well as commercially available composite sorbents based on modified activated carbons. Several natural mineral sorbents were selected (e.g. apatite, barite, bentonite) based on their low material cost and previous reports of use as sorbents. The other class of sorbents was engineered materials (e.g. ATS, Thiol-SAMMS) that are designed to have strong sorption capacity for specific metals.

Table 3. Selected materials tested for organic and heavy metal adsorption.

Adsorbent	Description	Form	Manufacturer	Price ($/ton)
Activated Alumina		P	Alcoa	4,000
Apatite	Phosphate mineral	G	Aurora phosphate mine	135
Amberlite	IX resin	B	Rohm & Haas	11,500-14,500
ATS	Cation exch. ceramic	P	Engelhard	Not Avail
ATC	AC w. ATS	G	Engelhard-Norit Am.	Not Avail
Barite	Barium sulfate mineral	G	Western stone produce, Inc.	200
Bentonite	Aluminum phyllosilicate	P	Wyo-Ben, Inc	200-1,500
Chitosan	Crab shell product polysaccharide	F		
ConSep CB-42%	AC w. IX resin	G	RICURA-Norit Am.	5$/lb
ConSep CB-20%	AC w. IX resin	G	RICURA-Norit Am.	6$/lb
GAC 30S (Base for ConSep CB)	Activated carbon	G	Norit Am.	3,200
Th-SAMMS	Thiol functionalized mesoporous silica	P	Steward Environmental Solution Inc.	$300/lb for small quantities, not known for large volume

B = Bead; G = Granular; F = Flake; P = Powdered; NE* = Not evaluated by manufacturer

Task 2: Measure sorption capacity for selected organic and inorganic contaminants. Where sufficient information on sorption capacity of a single amendment was not available, sorption isotherm tests were conducted for organic and metal contaminants. Early on in the selection

process it was determined that the most suitable sorbent for hydrophobic organics is activated carbon. Other carbon types such as coke, charcoal, and organoclays have been suggested, but the sorption capacity for PCB and PAH in activated carbons are at least an order of magnitude higher than in the other sorbents. As shown in Figure 1, the sorption capacity of activated carbon for different PCB homologs is nearly 3 orders of magnitude greater than that of coke. The difference in sorption capacity is largely due to the much higher specific surface area of activated carbons compared to other carbonaceous substances. Thus, a most likely combination of sorbents would be an activated carbon combined with a metal adsorbent. A range of pH adsorption edge experiments were conducted with the selected sorbents and sorbent combinations shown in Table 2. The sorbents were also evaluated for organic adsorption capacity using the industry standard Iodine Number test. The ASTM standard test method (D 4607) for determination of Iodine Number was performed primarily for the selection of materials for organic pollutant sorption.

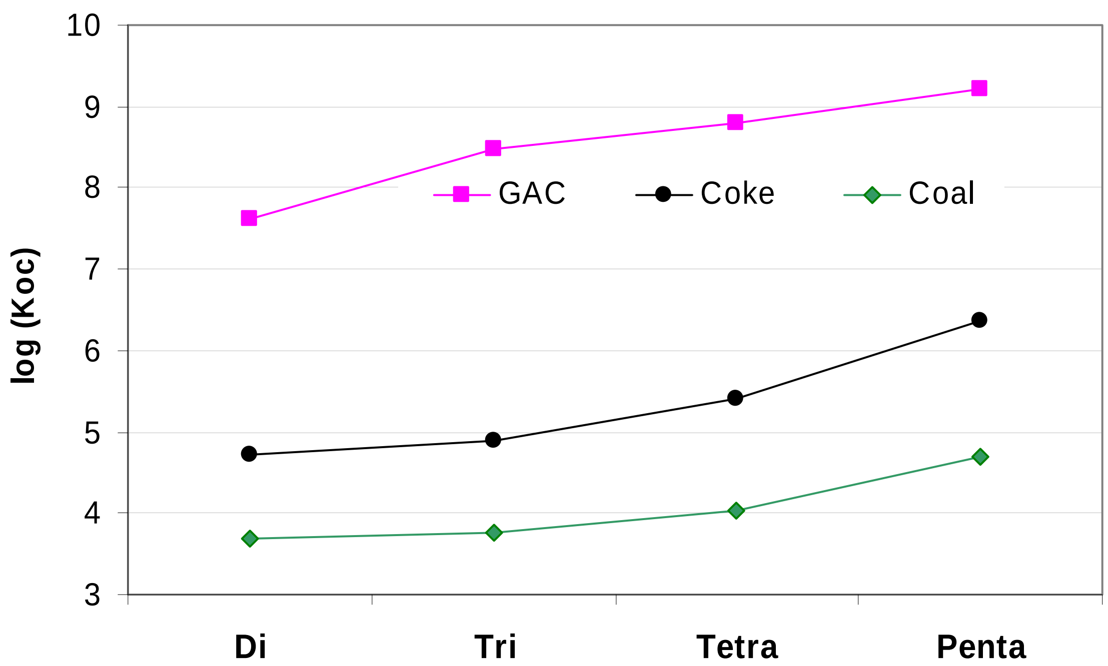

Figure 1. Measured log Koc values of three PCB homologs for coal, coke and activated carbon.

Heavy metal sorption studies. pH adsorption edge results for Cd and Pb are illustrated in Figures 2 (a) and (b). Figure 2 (a) shows the two Consep C materials (20% and 42% loaded) had very high removals above a pH value of 6. Cd removal by ATC increased from ~20% to 80% over the pH range 4-10. ATS removed nearly 100% of Cd after around pH 7. Activated alumina removal of Cd increased from 10% to nearly 80% over a pH range of 6-7.5. Pb results were similar, though slightly less clear, with the two Consep C materials displaying a clear pH adsorption edge at pH ~ 4.5-6, and ATS removing nearly 100% above pH 7. These results have shown that the two Consep C materials, and their base material, GAC30S, along with ATC, ATS, and activated alumina, have the greatest heavy metal removal capacities at a pH range of 6 – 7. Th-SAMM exhibits over 90 % removal for all tested pH range for both Cd and Pb. These materials were chosen for further isotherm studies.

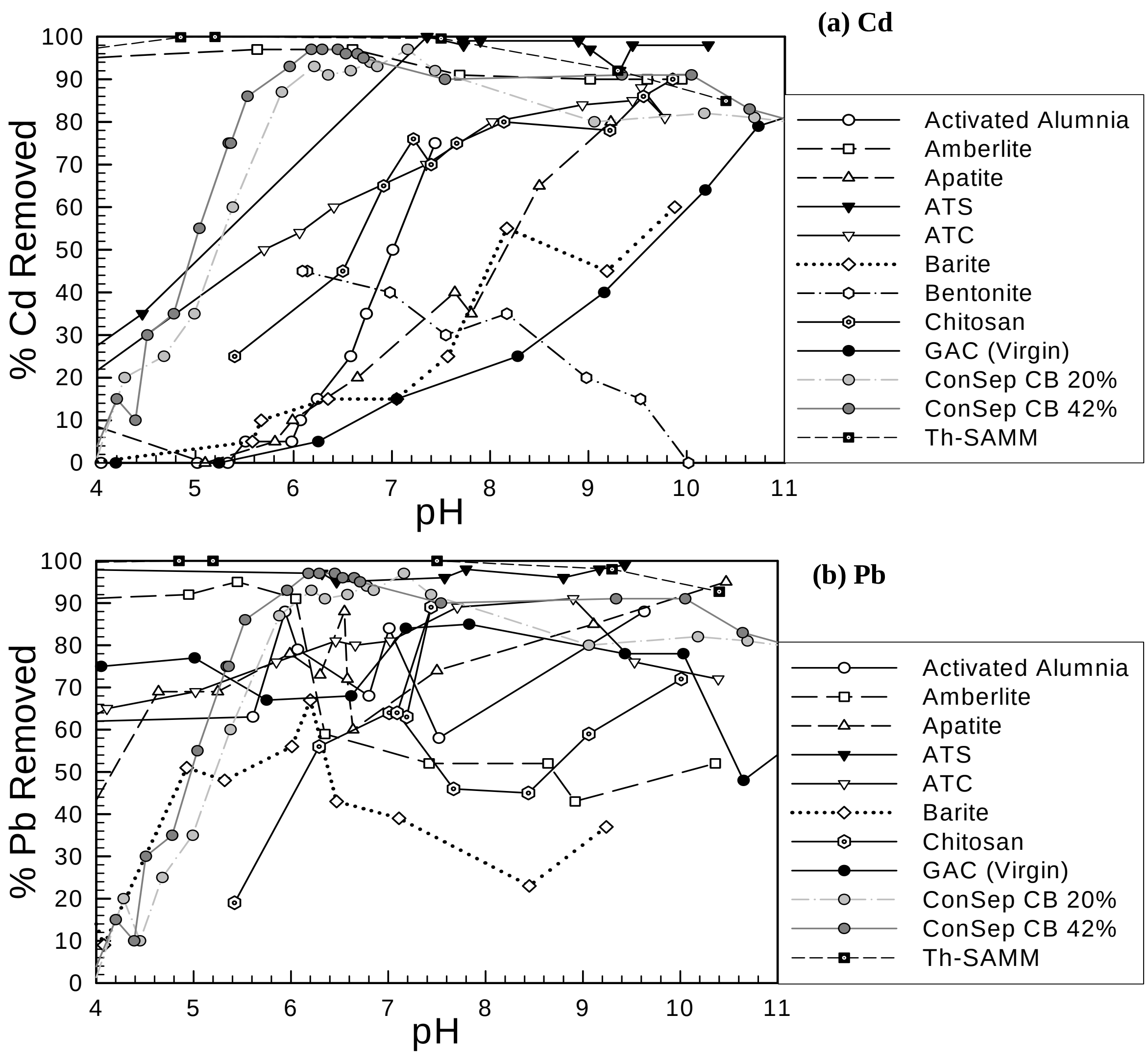

Figure 2. pH adsorption edge for cadmium (a) and Lead (b).

Organic Sorption Capacity by Iodine Number. Iodine Number tests have been regarded as an industry wide standard for measuring sorption capacity of activated carbons. The iodine number of a material, which is the amount of iodine (in mg) adsorbed per gram of material used, is a relative indicator of porosity and an approximation of surface area available for adsorption. This set of experiments provided a simple process for acquiring accurate data that can be used to compare and select materials for further testing. The ASTM standard test method (D 4607) for determination of iodine number was followed. The materials tested were granular activated carbon (GAC), alumina powder, ATS, apatite, bentonite, barite, ConSep 20 and 42%, and ATC. The Iodine Number measured for each sorbent is shown in Figure 3. Granular activated carbon (GAC) shows the highest iodine number among the sorbents tested. The iodine number measured for GAC was within the range of values typically reported for activated carbons. The absorption capacity of the ConSep carbons was not much lower than GAC which is the base material of the ConSep carbons. The 42% and 20% impregnation of ion-exchange resin to the GAC did not lower the sorption capacity of iodine too much. This shows the ConSep carbons as having promise for the sorption of both organics and metals. As shown earlier, the ConSep carbons work well in the uptake of metals (Cd and Pb). The sorption capacity of ATC was not much lower than GAC which is the base material. ATC is a composite of ATS which is a ceramic material engineered for the treatment of lead contaminated waters. The results of the iodine test show that ATC may do well for treating PCB and PAH contaminated sites as well as metals. Mersorb and HGR demonstrated about half the iodine number compared to activated carbon. The mineral materials (barite, bentonite, and apatite) did not have much sorption capacity for iodine, however they do show some metal sorption characteristics.

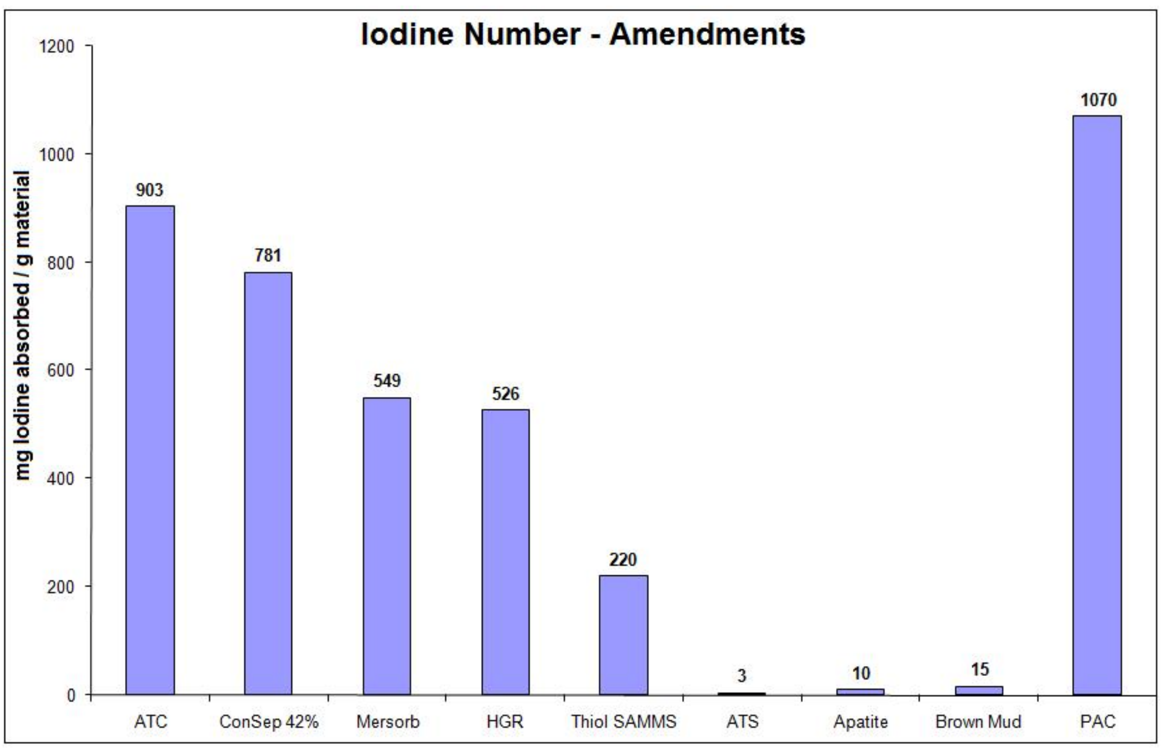

Figure 3. Iodine Number (mg I /g sorbent**) measurements for the selected sorbents. The results show that sorbents containing activated carbon (**ATC, ConSep 42, Mersorb, and HGR**) retain high iodine numbers.**

Task 3. Evaluate functional interactions between sorbents.

This task interpreted the data collected in Task 2. Sorption data for single amendments and amendments in mixtures were compared to evaluate interactions. The goal of this research was to be able to combine sorbents into mixtures to provide the range of sorption properties needed to address multiple contaminant types. Nonetheless, we recognize that it is possible that the presence of one sorbent type may enhance or impair the function of another sorbent type. A simple form of impairment could be through the physical blockage of sorption sites on one sorbent by the other (e.g., activated carbons amended with ion exchange resins or iron oxide coatings may enhance sorption capacity for metals, but could result in less available surface area for the sorption of organic contaminants). The iodine number results (Figure 3) for the two commercially available amended carbons (ATC and ConSep) indicate that the organic adsorption capacity of the carbons is marginally impacted by the incorporation of the metal adsorbing amendments. For example, pure activated carbons have an iodine number in the range of 800-1100 whereas, ATC, which is activated carbon with titanosilicate embedded in it, has an iodine number of 903. The results thus far suggest that multifunctional amendments may be functionally independent.

The iodine number test was used to determine if the binding material would interfere with the effectiveness of the carbon to adsorb contaminants when formed into pellets. The test uses iodine as a surrogate for organic chemicals such as PCB which are the target contaminants. The binding material for the carbon pellet was bentonite clay. The test was performed using a pellet combination of 60% PAC, 20% bentonite, and 20 % sand. This combination was chosen based on the results from physical tests. The average amount (in milligrams) of iodine adsorbed per gram of bentonite, expressed as X/M (mg/g), was 13. Figure 4, shows the results of the iodine test. The average iodine number for 1 gram of PAC in this experiment was 1082, and the average iodine number for the pellet mass which contained 1 gram of PAC was 1073. These results show that bentonite did not significantly interfere with the ability of PAC to adsorb iodine. Therefore, the bentonite is not expected to interfere with the ability of PAC to adsorb organic contaminants from sediment.

Similar tests were performed with the amendments used in the metal analysis. Results from these tests, shown in Figure 3, indicate that the amendments whose base material is activated carbon (HGR, Mersorb, ATC, Consep 42%) have iodine numbers close to activated carbon by itself (after accounting for percent carbon in the material). The ConSep carbon have relatively high numbers showing that the impregnation of ion-exchange materials did not have an overwhelming affect on the carbon's ability to absorb iodine. Alumina powder and ATS which are essentially ceramic materials show low iodine numbers.

Figure 5 shows the iodine number results of the amendments incorporated into the pellets. The amount of metal sorbent and the amount of activated carbon were equal for all the tests. When normalized to the amount of activated carbon in the pellets, the results show that the amendments do not hinder the carbon's sorptive ability. ATC, ConSep, Mersorb, and HGR, whose base material is activated carbon, showed increased sorption of iodine compared to activated carbon alone due to the contribution of the carbon present in the metal sorbent additive.

Results presented later under Task 5 also indicate that sorbent amendments applied simultaneously do not negatively interact. For example, results shown in Figures 17 and 18 with field sediment from Peninsula Harbor indicate that the presence of activated carbon and Thiol-

SAMMS together in the sediment matrix did not adversely impact performance. In fact, Thiol-SAMMS attributed additional sorption of PCB in the sediment matrix and activated carbon attributed additional Hg sorption when the two sorbents were added together. The interaction effects between sorbents were so small that further modeling of the interaction was deemed unnecessary.

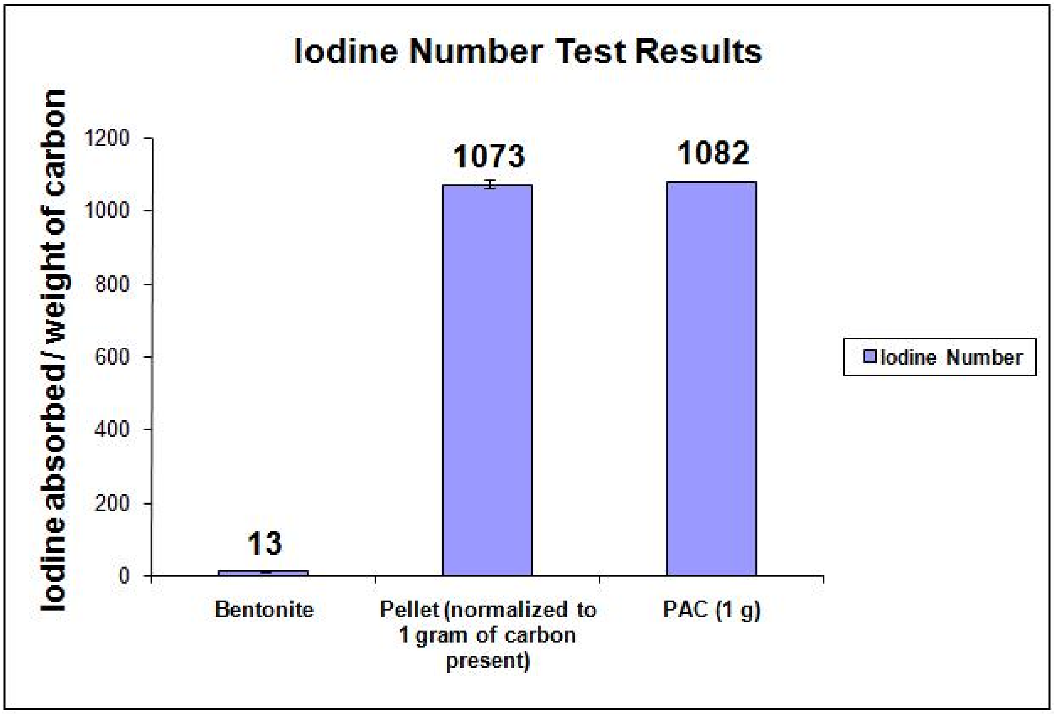

Figure 4: Iodine Number Test Results. The results from the iodine number test show that the presence of bentonite does not affect the ability of the carbon incorporated into the pellet to adsorb iodine. The iodine number of the pellet is within 1% of the iodine number of the carbon itself. Y-axis is in mg iodine/g carbon.

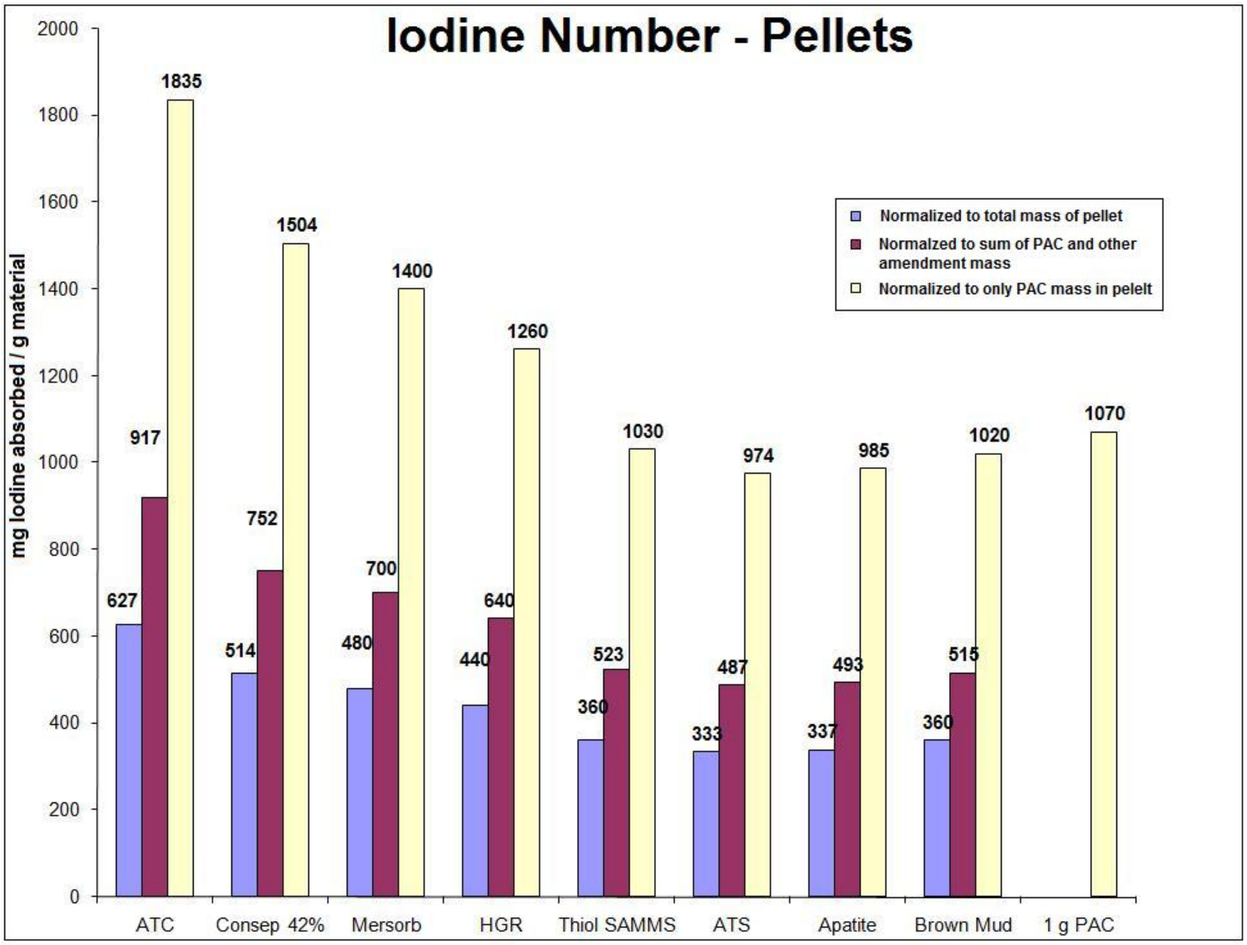

Figure 5. Iodine number test results for composite amendments incorporated into the pellet form. For each composite, the ratio of PAC and other amendment is 1:1. Results show that the presence of the amendments does not hinder the carbon's ability to absorb the iodine. In the case of amendments already containing activated carbon, the amount of iodine absorbed is more than that sorbed to PAC alone.

Task 4. Adapt traditional material science techniques to create amendment mixtures and composites and prUSEPAre a decision matrix for single and/or composite mixtures.

The two primary drivers for sorptive interactions between a sorbent and a sorbate are the abundance of surface functional groups responsible for binding interactions and easily accessible surface area. We have demonstrated the importance of available surface area in our work with in-situ stabilization of PCB in sediments using activated carbon amendment (9). Finer size carbon was found to be much more effective in reducing PCB aqueous concentrations in contact with sediment. However, the addition of powdered carbon or powdered metal sorbent to sediments may be problematic due to the possibility of entrainment into the water column. We adapted traditional material science techniques to create amendment mixtures and composites that have the necessary physical stability, sorptive/destructive properties, and mass transfer properties for application to sediment environments.

Two big challenges being faced in the application of the technology in the field are: 1) delivering the low-density carbon amendment into the sediment without losses of the carbon into the water column by resuspension, and 2) mixing the carbon into the top bioactive layer without causing a major disruption in the sediment consolidation and a release of suspended sediments into the water column. To make the in-situ bioavailability reduction approach successful, there is a great need to develop less intrusive and low-cost techniques to deliver the carbon and other sorbents and mixing the sorbents into the bioactive zone in the sediments. Our work addressed these two challenges by developing composite sorbent material pellets that have the right density and structural integrity to withstand delivery of the amendment through the water column without entrainment away from the target sediment. The composite materials were also designed to breakdown over time in the sediments to release the sorbent carbon allowing natural benthic mixing processes such as bioturbation and wave action to slowly mix the sorbent into the bioactive zone in the sediments. The purpose of the low-impact delivery system is to deliver the treatment materials directly to the water column and to forgo the more expensive and disruptive alternative of mechanical mixing and/or injection. Instead, the technology relies on natural biomixing (bioturbation) processes to mix treatment agents into the biologically active zone. The technology relies on “packaging” and delivering the treatment agent within a dense granule that is able to resist resuspension and that would be worked into the sediment by the organisms.

The development of the agglomerate involved testing a variety of materials for the ability to form the agglomerate using scalable laboratory techniques, testing the physical characteristics of the resulting agglomerates, and testing the interaction of the activated carbon and other agglomerate additives. Agglomerates were developed with the following properties: dense enough to sink through the water column and provide a light non-suffocating layer on the sediment, dense enough to be resistant to resuspension over the period it takes to be worked into the sediments, and able to break down to release active agents over the period of days to weeks. In addition, the binders used for the agglomerate were non-toxic. The most promising formulation was made of powdered activated carbon, bentonite clay, and sand as shown in Figure 6, and was produced in larger quantities for use in biological tests. The clear advantages of this over conventional systems are that it targets the biologically active zone where the benthic organisms reside, is less destructive of benthic habitats, can be used to augment removal and monitored natural restoration projects. Further, because the delivery system is relatively straightforward and has low impact, applications can be repeated, as needed, over time. We have added selected metal sorbents (e.g. Thiol-SAMMS) to the agglomerate mixtures to develop new materials that may be used to stabilize organics and metals in sediments.

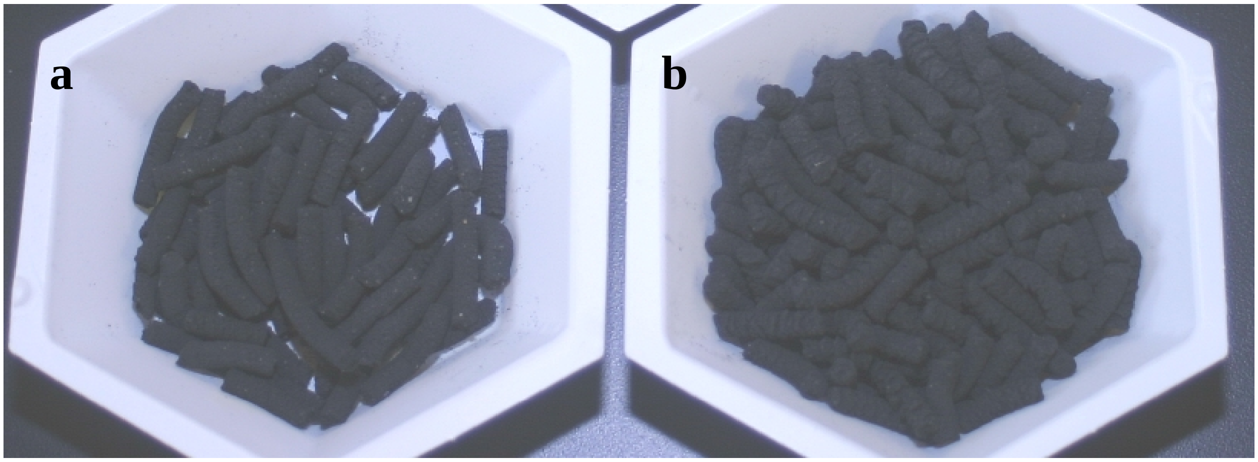

Figure 6. Sample images of produced agglomerates: a) 55% powdered activated carbon, 25% bentonite, 15% sand, 5% cellulose; b) 60% powdered activated carbon, 20% bentonite, and 20% sand.

Microcosm studies were conducted to evaluate the behavior of freshwater oligochaetes in sediment amended with PAC/bentonite/sand pellets. PCB-impacted sediment from Grasse River, NY and the freshwater oligochaetes *Lumbriculus variegatus* were used in these studies. Sediment (100 ml) and oligochaetes were placed in 400 ml glass beakers in triplicate. The control beakers contained sediment only and the treatment beakers has sediment covered with pellets at a dose to achieve 2.5% AC based on sediment dry weight. Figure 7 shows the surface of sediment with pellets before the addition of the oligochaetes and after 3 days of bioturbation by *Lumbriculus*. A close-up image of the sediment profile shown in Figure 8 illustrates the process of the breakdown of the pellets and incorporation into the bioactive layer of freshwater sediments. The process of bioturbation is illustrated well in Figure 8 showing the buildup of worm feces on top of the added pellets on the sediment surface. These studies also indicate that the pellet amendments are apparently non-toxic to the freshwater oligochaetes, and do not impair their normal feeding behavior when placed as a layer on the sediment surface.

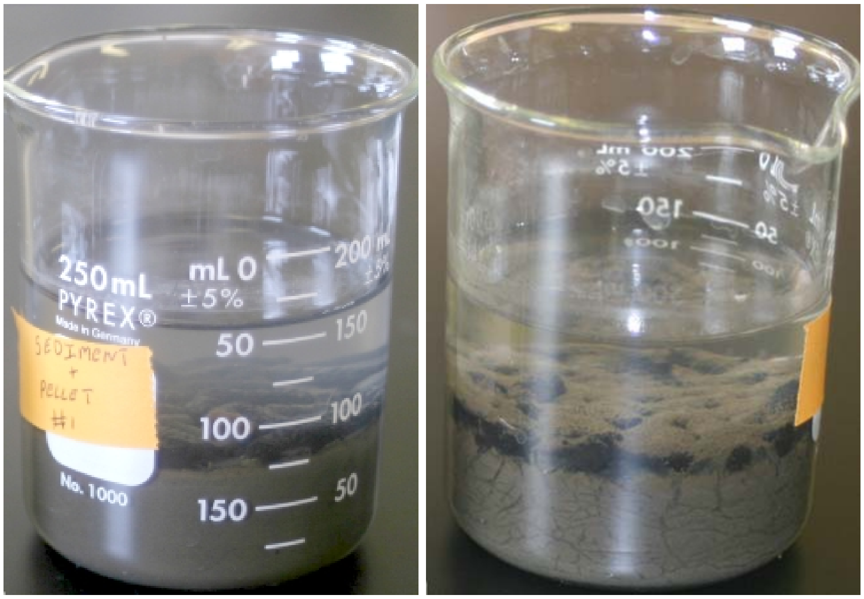

Figure 7. Picture on the left shows the placement of a layer of PAC/bentonite/sand pellet on Grasse River sediments and the picture on the right shows 3 days of activity of *L. variegatus* that produced a layer of worm feces on top of the layer of pellets starting the process of slow incorporation of the amendment into the top layer of sediments.

Figure 8. A close-up image of the sediment profile showing the buildup of worm feces (in 7 days**) on top of the amendment pellets and the slow incorporation of the pellet materials through the worm burrows.**

A bioaccumulation study was also conducted with PCB contaminated sediment from the Grasse River in New York to evaluate the effectiveness in reducing the bioaccumulation of PCB in benthic organisms by applying activated carbon to the sediment with two different application modes, pellet form and layer of powdered carbon. Two tests were conducted with the duration of the tests being 10 and 28 days after which the worms were collected and analyzed as stated in the methods section. The amount of carbon added as a thin layer on top of the sediment was 3.0% in the 10 day test and 2.0 % in the 28 day test. The total PCB reduction for both experiments is shown in Figure 9 (A – 10 days, B – 28 days) for total PCB and figure 10 for PCB homologs. Both experiments resulted in a decrease in the bioaccumulation of PCB in the test organisms and the results seem to be very reproducible. In each experiment, the carbon incorporated as a pellet was shown to be as effective at reducing the bioaccumulation of the PCB as the carbon by itself as a layer on top. This shows that the pellets can break down and be mixed effectively into the active layer by bioturbation. Though the amount of carbon incorporated in the 28 day test was lower than the amount in the 10 day test (2% vs. 3%), the reduction was greater (55% vs. 40%). This task demonstrates that the pellets can breakdown in a reasonable amount of time and that benthic life can potentially drive the mixing process of the pellet. If successful, this technology can lead to reduction of remediation costs and energy. Sensitive ecosystems could be addressed without disruption, and current strategies including capping could be merged with his technology to manage residuals.

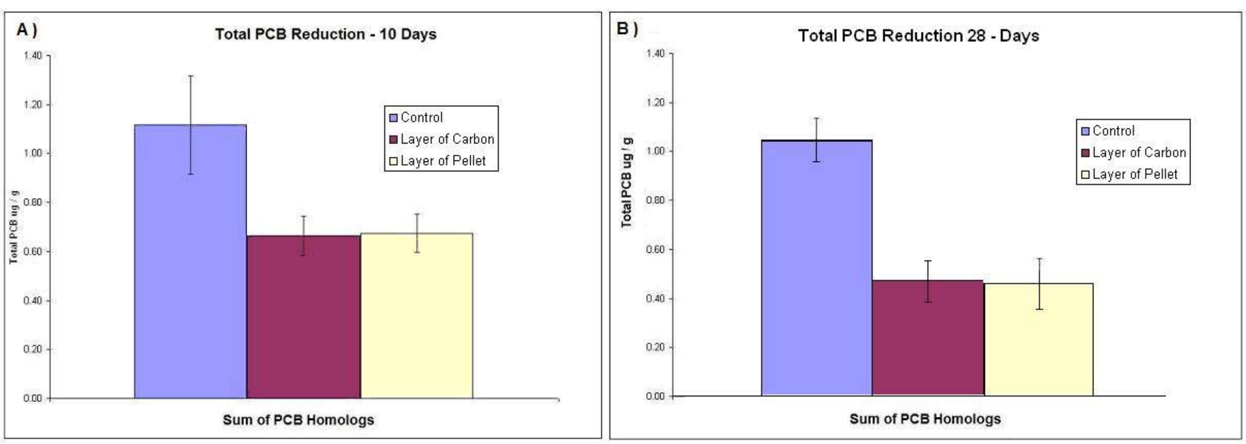

Figure 9. Concentration of total PCB in worm tissue for untreated sediment and sediment treated with different activated carbon modes. The 10-day test (shown on left**) received a dose of 3% activated carbon by dry weight, and the 28-day test (**shown on right**) received a lower dose of 2% activated carbon by dry weight.**

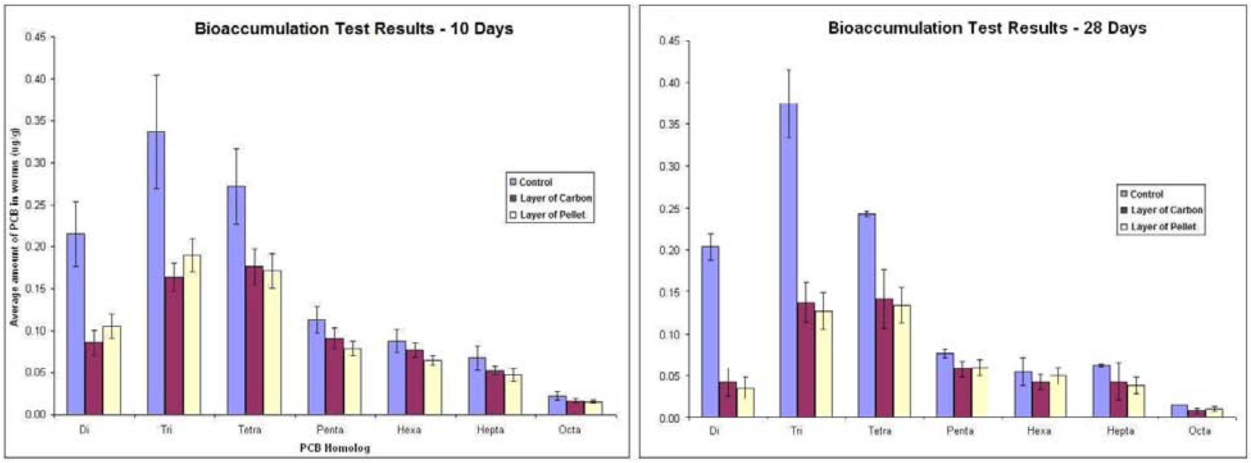

Figure 10. Concentration of PCB homolog in worm tissue for untreated sediment and sediment treated with different activated carbon modes. The 10-day test (shown on left**) received a dose of 3% activated carbon by dry weight, and the 28-day test (**shown on right**) received a lower dose of 2% activated carbon by dry weight.**

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Task 5: Evaluate technology using field sediments

I) Chronic toxicity testing of sediment amendments. This task evaluated potential deleterious effects of the selected amendments on organisms in benthic environments. The selected sorbents were ATS, Thiol-SAMMS and HGR that were selected for biouptake studies for Cd, Pb and Hg and also ConSepC and red mud were included due to their potential as sorbents for other metal contaminants. Table 4 illustrates the survival of three benthic organisms (*Chironomus dilutus* (a), *Hyalella Azteca* (b) *and Leptocheirus plumulosus*(c) in the amendment treated sediments. Table 6 illustrates survival for *Neanthes arenaceodentata*. Effects of sorbents on invertebrate biomass were also evaluated and the results are shown in Tables 4 and 7. These tests were conducted at the ERDC with clean freshwater (Brown's lake, Vicksburg, Mississippi) and marine (Sequim Bay, Washington) sediments. The dose of amendments used in the toxicity assessments was 5% by dry weight. Test organisms included two sensitive freshwater species and two sensitive marine species:

1) *Chironomous dilutus* 20-d survival and growth
2) *Hyalella azteca* 28-d survival and growth
3) *Leptocheirus plumulosus* 28-d survival, growth, and reproduction
4) *Neanthes arenaceodentata* 28-d survival and growth.

In general, most amendments proved to be nontoxic in chronic exposures and bioactivity was not diminished by 28-day exposure to amended sediment.

As shown in the attached tables, there were no statistically significant effects of the Thiol-SAMMS amendment on the survival and growth of *C. dilutus*, *L. plumulosus*, and *N. arenaceodentata*. In addition, reproduction of *L. plumulosus* and the growth of *H. Azteca* were not affected. The only statistically significant impact observed was that of survival of *H. Azteca* where there was a significant 25% reduction after amendment of sediment with Thiol-SAMMS.

All other amendments were not statistically different from the control for all endpoints evaluated. Although not statistically significant, the lowest survival observed for *C. dilutus* and *L. plumulosus* were also observed in the Thiol-SAMMS amended sediments (Table 4 (a) and (c)). The survival effect observed for *H. Azteca* may be related to the average approximate particle size of 40 µm of the Thiol-SAMMS amendment. Kennedy et al (41)demonstrated a 67% reduction in *H. Azteca* survival when exposed to an activated carbon amendment rate (2.9%) similar to the current study, albeit the size of the particles was less than 38 µm. Sediment toxicity identification evaluation (TIE) Guidance (42) also indicates that effects on survival with *H. Azteca* are likely when using carbon with particle size of <45 µm and exceeding a 2% amendment wet weight to sediment wet weight ratio. These data strongly suggest increased *H. Azteca* sensitivity as particle size decreases. The cause of particle size induced toxicity is unclear but may be due to physical effects such as occlusion of the gill resulting in suffocation (43, 44). Increasing the particle size of Thiol-SAMMS may eliminate the observed toxicity. In addition, the apparent toxic effect of Thiol-SAMMS in *H. Azteca* should be considered in conjunction with the potential benefit of its ability to reduce mercury bioavailability and toxicity. The toxicity observed for Thiol-SAMMS was moderate with a reduction in *H. Azteca* survival from 98% to 73%. Although Thiol-SAMMS reduced survival, it may increase survival in mercury

contaminated sediments from much lower levels of survival (<73%) to levels that would be deemed acceptable for meeting remediation goals. For example, *L. plumulosus* survival in diluted Augusta Bay (contaminated) sediment was 24% compared to a survival of 69% in the same sediment after amendment with Th-SAMMS. Results of *L. plumulosus* reproduction (neonates/survivor) following 28-d exposure to amendments are shown in Table 8.

Table 4. Percent survival of *C. dilutus* (a), *H. Azteca* (b) and *L. plumulosus* (c) following 28-day exposure to control and amended sediments. Values with * were obtained from a separate study.

(a)

Treatment	Mean survival (%)	Stdev (%)	C.V (%)	n
Control	98.6 (76.4*)	3.4 (20.0*)	3.4 (26.2*)	6
ATC	93.1	8.2	8.8	6
ATS	100	0.0	0	6
ConSep	95.8	4.6	4.8	6
Redmud	100	0.0	0	6
HGR	84.7*	6.3*	7.4*	6
Th-SAMMS	68.1*	11.1*	16.3*	6

(b)

Treatment	Mean survival (%)	Stdev (%)	C.V	n
Control	88.3 (98.3*)	9.8 (4.1*)	11.1 (4.2*)	6
ATC	86.7	19.7	22.7	6
ATS	83.3	13.7	16.4	6
ConSep	91.7	9.8	10.7	6
Redmud	88.3	11.7	13.2	6
HGR	96.7*	21.6*	29.5*	6*
Th-SAMMS	73.3*	5.2*	5.3*	6*

(c)

Treatment	Mean survival (%)	Stdev (%)	C.V (%)	n
Control	80	11.7	14.7	5
ATC	78	11.5	11.5	5
ATS	77	8.4	8.4	5
Redmud	76	6.5	6.5	5
HGR	71 (78*)	9.1	9.1	5
Th-SAMMS	71	11.9	11.9	5

Table 5. Produced biomass of *C. dilutus* (a), *H. Azteca* (b) and *L. plumulosus* (c) following 28-day exposure to control and amended sediments. Values with * were obtained from a separate study.

(a)

Treatment	Biomass (mg dry)	Stdev (%)	C.V (%)	n
Control	1.28 (1.31*)	0.33 (0.31*)	26.0 (23.4*)	6
ATC	1.51	0.38	25.5	6
ATS	0.98	0.19	19.8	6
ConSep	1.17	0.37	31.9	6
Redmud	1.20	0.28	23.1	6
HGR	0.94*	0.23*	24.1*	6*
Th-SAMMS	1.19*	0.29*	23.9*	6*

(b)

Treatment	Biomass (mg dry)	Stdev (%)	C.V	n
Control	0.46 (0.38*)	0.16 (0.06*)	34.4 (17.0*)	6
ATC	0.56	0.25	45.0	6
ATS	0.40	0.13	33.2	6
ConSep	0.39	0.07	18.6	6
Redmud	0.34	0.08	22.9	6
HGR	0.29*	0.04*	13.5*	6*
Th-SAMMS	0.29*	0.10*	33.2*	6*

(c)

Treatment	Biomass (mg dry)	Stdev (%)	C.V (%)	n
Control	1.47	0.15	10.5	5
ATC	1.27	0.22	17.7	5
ATS	1.63	0.17	10.4	5
Redmud	1.34	0.31	23.4	5
HGR	1.47	0.16	11.1	5
Th-SAMMS	1.27	0.42	33.9	5

Table 6. ***N. arenaceodentata*** **percent survival following 28-d exposure to amendments.**

Treatment	Mean (%)	S.D. (%)	C.V.	n
Control	100	0	0%	10
ATC	100	0	0%	10
ATS	80	42.2	52.7%	10
Conspec	100	0	0%	10
Redmud	100	0	0%	10
HGR	90	31.6	35.1%	10
Thiol-SAMMS	100	0	0%	10

Table 7. ***N. arenaceodentata*** **biomass (mg dry weight) following 28-d exposure to amendments. (**The two sets of experiments were conducted separately with different batches of organisms**)**

Treatment	Mean	S.D.	C.V.	n
Control	0.97	0.20	20.4%	10
Thiol-SAMMS	1.07	0.39	36.4%	10
HGR	0.98	0.26	26.7%	10

Treatment	Mean	S.D.	C.V.	n
Control	2.51	0.75	30.1%	10
ATC	2.33	0.89	38.3%	10
ATS	2.48	1.00	40.5%	10
Conspec	2.00	0.36	17.9%	10
Redmud	2.69	0.65	24.2%	10

Table 8. ***L. plumulosus*** **reproduction (**neonates/survivor**) following 28-d exposure to amendments.**

Treatment	Mean	S.D.	C.V.	n
Control	0.79	0.19	24.5%	5
ATC	0.80	0.92	114.8%	5
ATS	0.48	0.21	43.3%	5
Redmud	0.55	0.26	46.9%	5
HGR	0.33	0.28	84.6%	5
Thiol-SAMMS	0.69	0.21	29.9%	5

ii) Bioaccumulation of Cd, Pb, Hg, and methylmercury in Anacostia River sediments. Based on the results from literature and aqueous phase sorption studies, Th-SAMMS and ATS were chosen for the stabilization of Cd and Pb, respectively, in sediments phase. A biouptake study was conducted with Anacostia River sediment with Cd and Pb to evaluate the effectiveness on the reduction of uptake by freshwater oligochaetes (*L. variegatus*). Figure 12 shows the concentration of Cd in the worm tissue under different amendments, none (control), GAC, and Th-SAMMS, at 5-day (a) and 90-day (b) contact times. In the untreated sediment (control), the tested worms showed the highest degree of Cd uptake regardless of the contact time period. The Cd concentration of worms from untreated control are similar to a literature value where L. variegatus was incubated in water with similar Cd concentration(36). About 82 % of biouptake reduction in Cd can be observed from the sediment amended with Th-SAMMS for 5 days. After 90 days, the level of Cd in worm tissue in the Th-SAMMS treatment is maintained at levels close to the 5-day treatment, while Cd uptake in unamended and GAC treated sediment increases. Aqueous concentrations of Cd in amended and unamended sediments are also shown in Figure 12. Amendment with Th-SAMMS reduced aqueous Cd concentration by 99.5% and 97.0 % in the 5-day and 90 day treatments, respectively, compared to control (unamended) sediment samples. Reductions in aqueous Cd concentration corresponds well with reductions in biouptake of Cd indicating that porewater concentration is limiting parameters for biouptake as demonstrated in previous studies (45, 46). Sequential extraction results (figure 13 (a)) indicate that 86.6% of spiked Cd in the control sediment was present as easily ion-exchangeable and weak acid extractable fractions in unamended sediment. Ion exchangeable Cd in the sediment was dramatically suppressed to 0.1 % of total extractable Cd (a 99.9% reduction) by the Th-SAMMS treatment. The other three sorbent amendments produced only a marginal shift in extractable fractions of Cd compared to the control. Total Cd recovery, which is the sum extracted by all procedures, for each amendment system is at least 92% compared to total Cd measured in the unamended sediment.

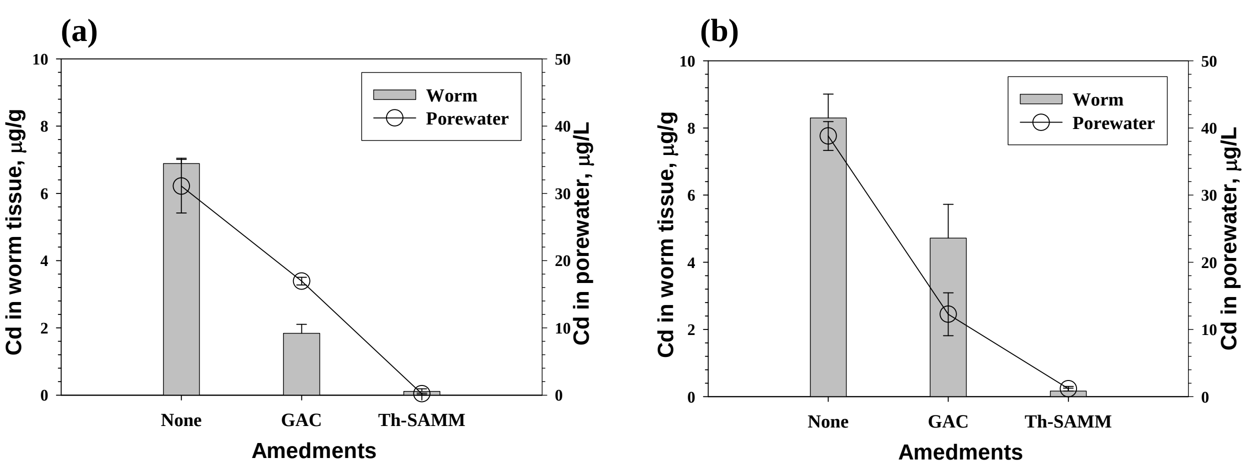


Figure 12. Reduction of Cd concentration in *L. variegatus* and porewater after sorbent addition to sediment for 5-day (a) and 90-day (b) contact periods. Th-SAMM and GAC dose was 4% by sediment dry wt.

The concentration of Pb in the worm tissue under none, GAC and ATS amendments are illustrated in Figure 14. The biouptake reduction of Pb with ATS treatment is not significantly different compared to control and GAC treatment. Unlike spiked Cd, the amount of Pb that is easily bioavailable is minimal. Pb concentration in the sediment was low and only 6.4 % was present in the readily bioavailable (ion exchangeable and weak acid extractable) fraction (Figure 13 b). Treatment with ATS and ATC decreased the reducible fraction and increased the residual fraction but did not result in bioaccumulation changes. Aqueous concentration of Pb in all samples was below detection limits.

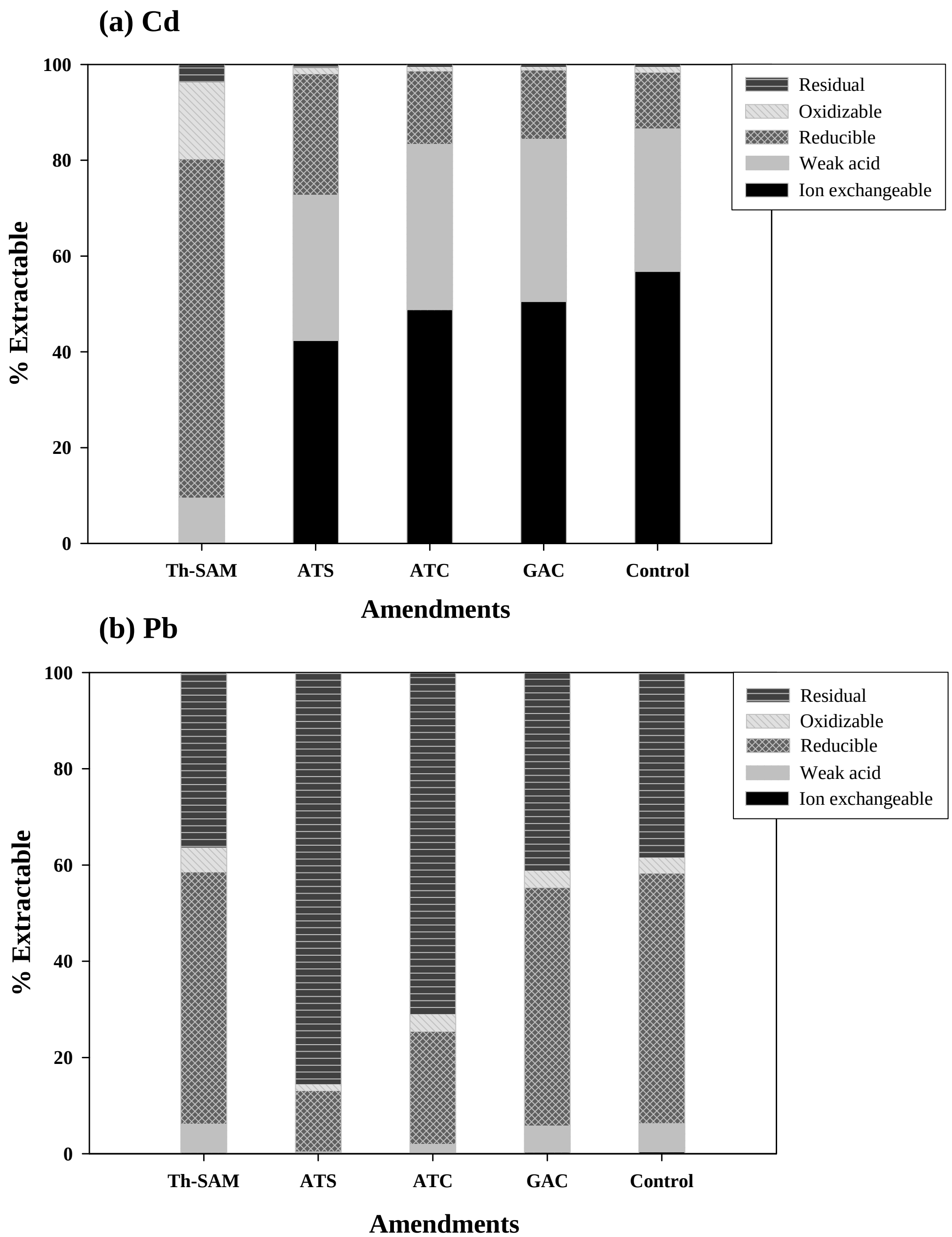


Figure 13. Percentage of extractable Cd (a) and Pb (b) found in sequential extraction procedure.

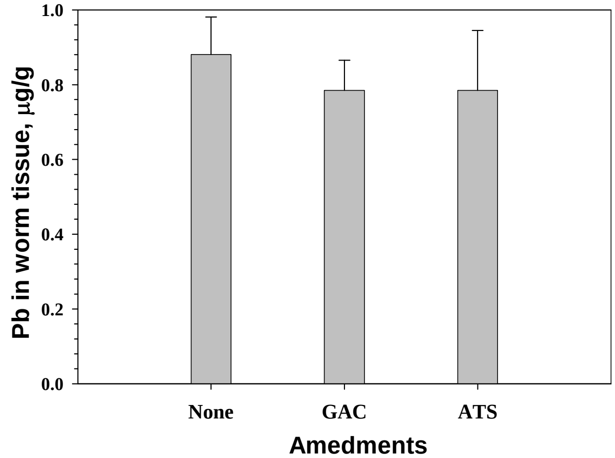


Figure 14. Pb concentration in *L. variegatus* after sorbent addition to sediment for 14-day contact periods. Th-SAMM and GAC dose was 4% by sediment dry wt.

A biouptake study was conducted with Anacostia River sediment with spiked Hg to evaluate the effectiveness of sorbents in reducing Hg uptake by freshwater oligochaetes (*L. variegatus*). Figure 15 shows the concentration of Hg in the worm tissue under amendment treatment, none (control), GAC, HGR, and Th-SAMMS, at 5-day (a) and 90-day (b) contact times. In the untreated sediment (control), the tested worms showed the highest degree of Hg uptake regardless of the amendment treatment time period. Total mercury biouptake was reduced by approximately 75% in sediment amended with Th-SAMM for 5 days. A 55 % and 35 % of Hg biouptake reduction were also achieved by GAC and HGR treatment, respectively, indicating that elemental sulfur on HGR may not provide additional Hg sorption in sediment. The 5 day Hg biouptake study was repeated using a set of sUSEPArate mesocosms (Figure 16) and the degree of biouptake reduction and the order of treatment effectiveness (Th-SAMMS > GAC ≈ HGR > Control) were well maintained. While approximately a factor of two increases in the worm concentration of Hg was observed for all treatments after 90 days, the Th-SAMMS treatment was still most effective compared to others. The effectiveness on biouptake reduction of methylmercury (MeHg) was also investigated in the mesocosms for total Hg biouptake study. Figure 17 illustrates MeHg concentration in worm tissue following 5-day and 90-day exposures. Methylmercury concentrations in all three treatment sediments were less than in the controls (ANOVA, $p < 0.1$) after 5-days of the treatment. Both activated carbon treatments decreased MeHg concentrations in worms by more than 60%; while the Thiol-SAMMS treatment resulted in a >85% reduction in MeHg concentrations in worms. Results of this task strongly suggest that the proper selection of amendment sorbents is essential for effective bioavailability reduction. Th-SAMMS is ideally suited for Cd and Hg sequestration in the contaminated sediments. Activated carbon shows moderate reduction in mercury biouptake but may be more cost effective than Th-SAMMS. ATS may also be effective in sediments where a larger bioavailable pool of Pb exists. All methylmercury measurements were performed by Dr. Cindy Gilmour at the Smithsonian Environmental Research Center. Partnership with Dr. Gilmour allowed for very low concentration measurements of methylmercury in sediment and biota and interpretation of mercury biogeochemistry.

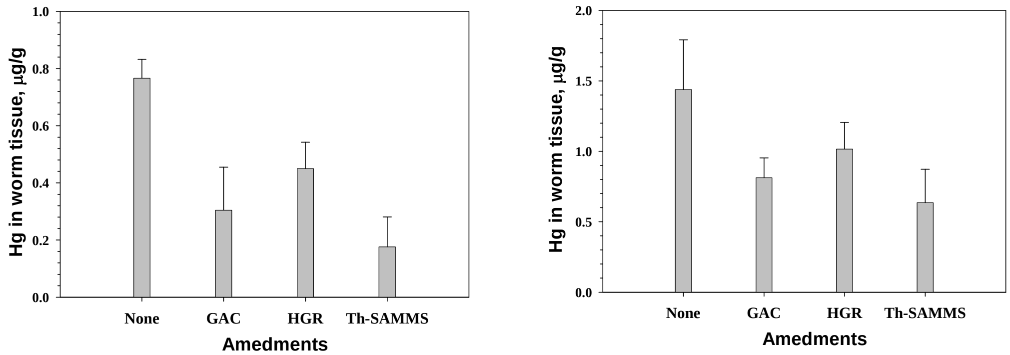


Figure 15. Concentration of total Hg in worm tissue after 5 (a) and 90 (b) days of amendments contact followed by 5-day exposure of worms.

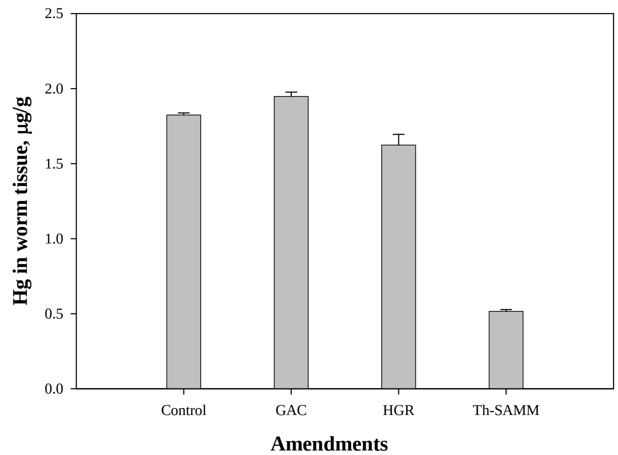


Figure 16. Concentration of total Hg in worm tissue after 5 days of amendments contact followed by 5-day exposure of worms measured by repeated experiments.

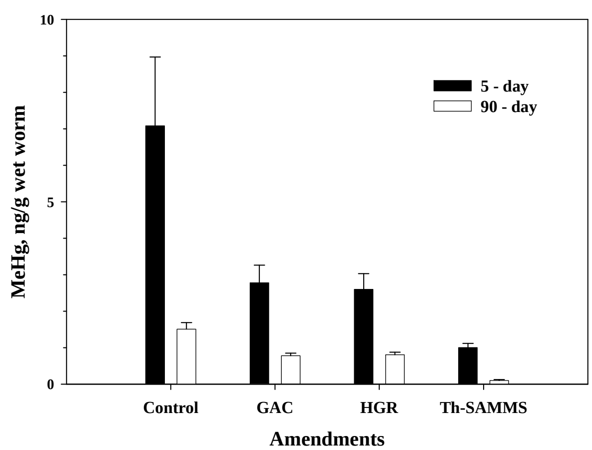


Figure 17. Methylmercury concentrations in worm tissues after 5 and 90 days of amendments contact followed by 5-day exposure of worms.

iii) Bioaccumulation of PCB, Hg, and methylmercury in Peninsula Harbor sediments:

In this task, the effectiveness of selected amendment mixtures in reducing bioavailability of multiple contaminants was evaluated using field sediment that is contaminated by both mercury and PCB contamination. Mercury is a contaminant of concern in Lake Superior's Peninsula Harbor on the Canadian shore. Mercury contamination in the sediment in these areas is due in part to historical discharges of mercury used as a fungicide in industrial applications, use of mercury reagents, and discharge by chlor-alkali plants. PCB is also among the sediment contaminants found at this sediment site.

Mercury in the sediment was extracted by acid digestion and determined to be 14.6 ±1.5 ppm (mg/Kg dry sed). This level of mercury contamination is higher than the apparent effect threshold (AET) concentrations (2.3 mg/kg) determined by amphipod survival test (47) and can be considered to be toxic. However, an initial five step sequential extraction test results (based on the methods described in Tessier et al, 1979 and Terzano et al, 2007 (39, 40)) indicate that more than 98 % of mercury in this sediment exists in the residual form which can only be extracted by a harsh acid treatment and the amount of mercury in bioavailable forms (i.e., ion-exchangeable and weak acid extractable) are negligible.

The concentration of PCB in the sediment was determined by the ultrasonic extraction method based on USEPA SW846-3550B and total PCB concentration was 1.1 ± 0.4 ppm (mg/Kg dry sed). The concentration distribution of each PCB congeners is presented in Figure 18. Hexa- and hepta chlorobiphenyls are predominant in the sediment.

Laboratory scale mesocosms were conducted to evaluate the effect of multifunctional amendments in simultaneously reducing the biological uptake of native PCB, Hg, and Me-Hg in sediment. For this study, AC was used for PCB binding. As an additional sorbent for mercury, Thiol-SAMMS was selected based on the previous results. Individual sorbents and sorbent mixture were amended to the sediment and allowed to equilibrate for a month before conducting bioaccumulation tests using freshwater oligochaetes (*Lumbriculus variegatus*).

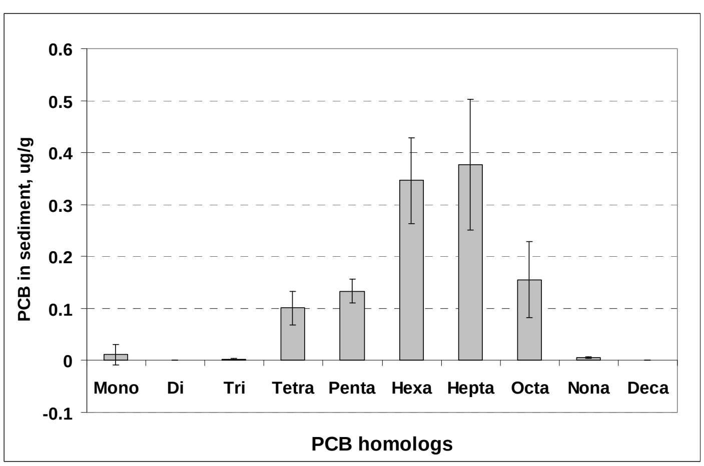


Figure 18. Concentration of PCB homologs in the Peninsula Harbor sediment.

Figure 19 shows the concentration of PCB homologs in the worm tissue incubated in untreated and treated sediment. For the untreated sediment, PCB homolog distribution in the worm tissue follows the homolog distribution observed in the sediments with hexa- and heptachlorobiphenyls forming the dominant congeners. Over 60 % reduction in biouptake is observed for total PCB in the 3% AC treated sediment. The sediment amended with 3% AC and Th-SAMMS demonstrated around 90% reduction in total PCB biouptake in the worm tissue. Best PCB biouptake reduction is found with the sediment treated by the mixture of AC and Th-SAMMS, indicating Th-SAMMS may serve as an additional sorbent for PCB in sediment environments.

Figure 20 illustrates the concentration of MeHg in wet worm tissue from the same mesocosms used for PCB biouptake described above. A significant biouptake reduction of Hg can also be observed. While about 30 % of biouptake reduction of MeHg was achieved by AC treatment, Th-SAMMS treatment alone or with AC resulted in over 90 % reduction. To our knowledge, this is the first demonstration of simultaneous bioavailability reduction of native PCB, Hg, and Me-Hg in sediments using multifunctional amendments.

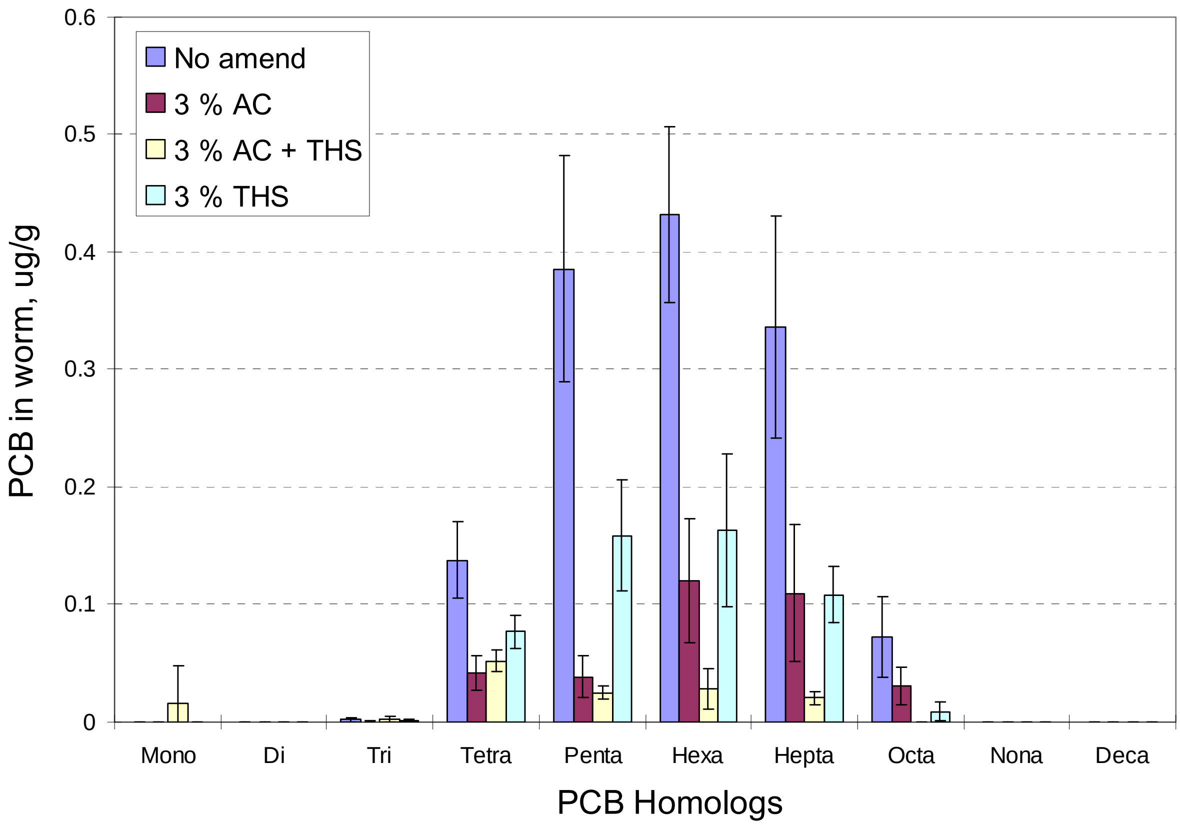


Figure 19. PCB homolog concentration in the worm tissue for untreated sediment and sediment treated with amendments.

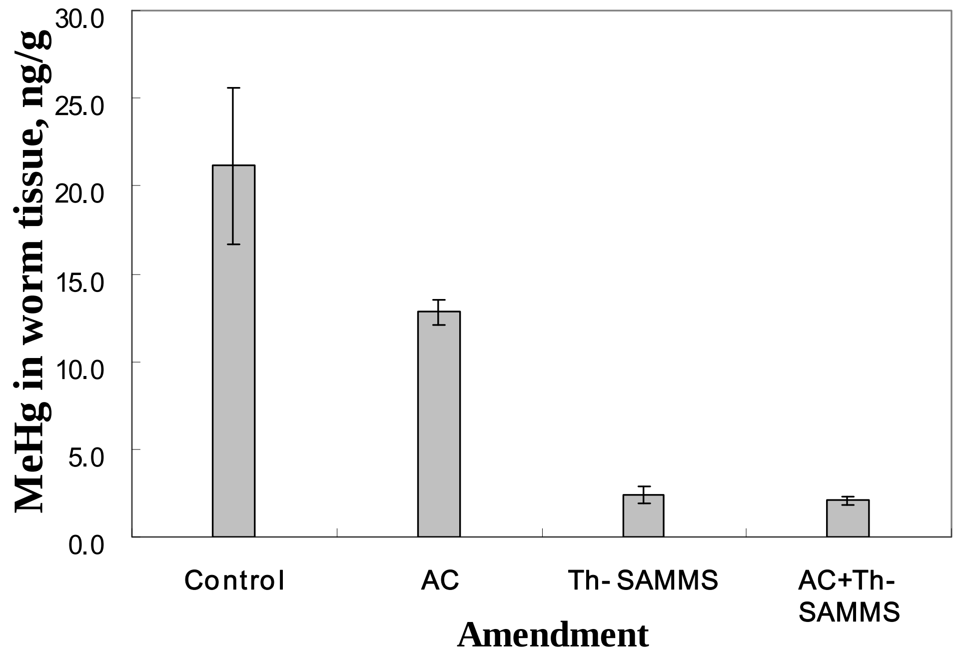


Figure 20. MeHg concentration in worm tissue for untreated sediment and sediment treated with amendments.

iv) Bioaccumulation of Hg and methylmercury in Augusta Bay, Italy sediment.

The mercury laden sediment utilized in the marine toxicity studies was collected from an industrial field site located in Sicily, Italy. The sediment contained a range of contaminants that exceeded their respective ER-M toxicity reference values including copper, mercury, 2-methylnapthalene, fluorine and phenanthrene. Sediment concentrations of these contaminants exceeded their ER-M by 3 orders of magnitude or less except mercury whose concentration was 525 times higher than the established ER-M suggesting that it is likely the primary driver of toxicity in the sediment. Total and methyl mercury concentrations in the sediment were 373 mg/kg and 9.52 ng/g, respectively. Sediment TOC was also high at 12.9%. The sediment used for dilution of the mercury contaminated sediment was collected from Sequim Bay (SC) (Sequim, Washington). The dilution sediment (SC) is routinely used as a performance control in routine toxicity and bioaccumulation studies at the ERDC. Based on survival results of a *Leptocheirus plumulosus* range finding study, a 1.2% dilution of the IT sediment was chosen as the baseline or control for evaluating the efficacy of the amendments. The 1.2% IT sediment was amended with activated carbon (AC) and Thiol-SAMMS (TS) at a 5% amendment dry weight to sediment dry weight ratio. An unamended or control sediment was included as a basis of comparison for determining the efficacy of the amendments to bind mercury. The required amount of sediment and amendment were weighed and placed in amber 1 gallon glass jar. The

contents of the jar were mixed by hand then placed on a rolling mill apparatus. The sediment was slowly rolled for 28 days in the dark at room temperature to ensure a homogenous mixture.

Although trends of decreased mercury bioaccumulation were evident, due to high variability in the data, no statistically significant decreases in mercury tissue residue levels were detected for the activated carbon and Thiol-SAMMS amendments relative to the control (Figures 21, 22 and 23). The apparent decreased total and methyl mercury tissue concentrations in the activated carbon treatment for *N. virens* were not statistically significant (Figures 21 and 22). No clear trend was evident for Thiol-SAMMS amendment treatment relative to the control in *N. virens*. A trend of lower bioaccumulation of methylmercury in the activated carbon and the Thiol-SAMMS treatments was evident in the *L. plumulosus* exposures with a greater apparent decrease in mercury tissue residues levels occurring in the Thiol-SAMMS treatment.

The results of the bioaccumulation studies with diluted Augusta Bay sediments are difficult to interpret due to poor survival of one of the organisms in the untreated sediment. While the survival of *N. virens* in the bioaccumulation test was not significantly different among the treatments, *L. plumulosus* showed poor survival in the untreated sediment. *L. plumulosus* survival in diluted Augusta Bay sediment was 24% compared to a survival of 69% in the same sediment after amendment with Th-SAMMS. The low survival of *L. plumulosus* in the untreated sediment may indicate poor health/low feeding rate in the untreated sediment that may reduce bioaccumulation in the untreated sediment. We also believe that the near 100-fold dilution of the original sediment to clean sediment may have resulted in a heterogeneous distribution of the mercury contamination among the treatments. The final Hg concentration in the diluted sediment matrix was not evaluated.

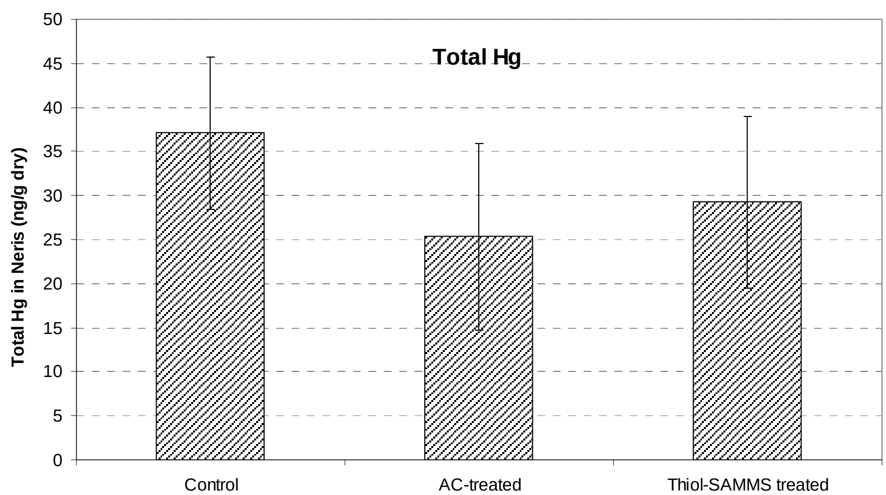


Figure 21. *Neires virens* total mercury tissue concentrations (ng/g) following a 28-d exposure.

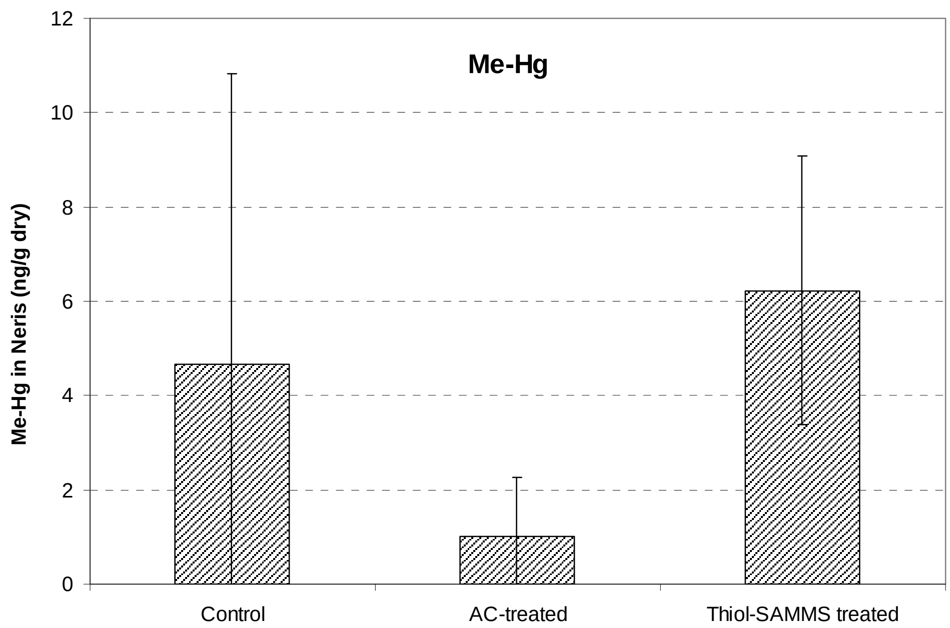


Figure 22. ***Neires virens*** **methyl mercury tissue concentrations (ng/g) following a 28-d exposure.**

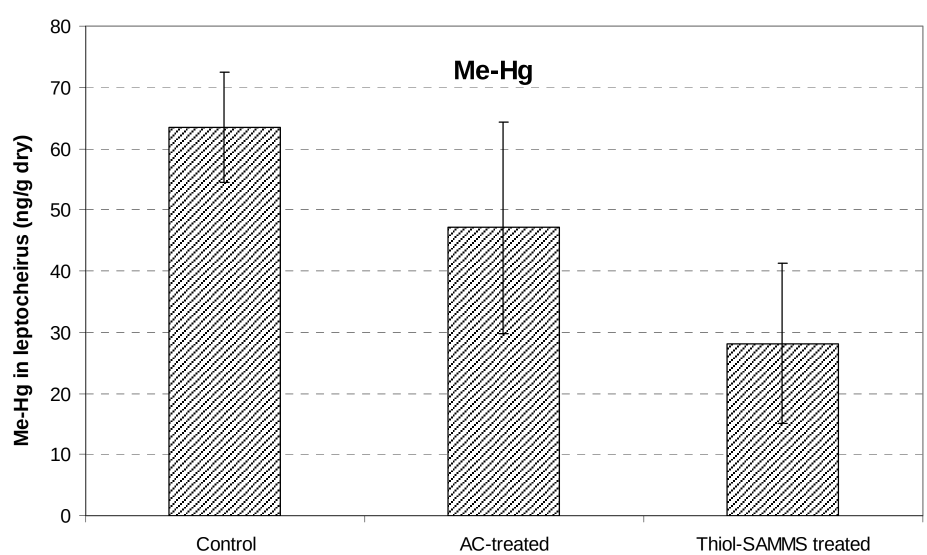


Figure 23. ***Leptocheirus plumulosus*** **methyl mercury tissue concentrations (ng/g) following a 28-d exposure.**

v) Bioaccumulation of Hg and methylmercury in River sediment.

During the course of study, an organoclay developed as a mercury adsorption media, by CETCO was obtained for inclusion as potential mercury sorbent. This material, MRM, has demonstrated its effectiveness in the removal of mercury in wastewater remediation applications and in soil solidification/stabilization applications as an additive to cement-based treatment. Due to ineffectiveness in Hg biouptake reduction, HGR was replaced to MRM for the bioaccumulation test using sediment from a river in Virginia impacted with historic Hg releases. Figure 24 presents total and methyl mercury concentration in *L. variegates* tissue after 14-days of exposure to control and treated sediments. Compared to the control, Th-SAMMS and GAC treatment achieved 77% and 84% reductions in total Hg biouptake in the worms. For Methylmercury, the bioaccumulation reductions were greater with 96% and 90% reductions for Th-SAMMS and GAC treatments respectively. MRM was not as effective as GAC and Th-SAMMS in the reduction of methylmercury and total mercury in the worms. The degree of the Hg biouptake reduction corresponds well to those of porewater concentration of mercury (Figure 25). Th-SAMMS and GAC reduced the bioaccumulation factor of methyl mercury in sediment by 95% from a value of 15 to 0.6. Results from these tests indicate that methylmercury formed in the sediment become much less bioavailable in the presence of strong sorbents such as Th-SAMMS and GAC. In this case, GAC demonstrated the best performance in the reduction of mercury in both biouptake and porewater, which may be due to abundance of the organic form of mercury in the sediment pore water so that physisorption to GAC surface is dominant rather than ligand binding, the mechanism of mercury binding to Th-SAMMS surface.

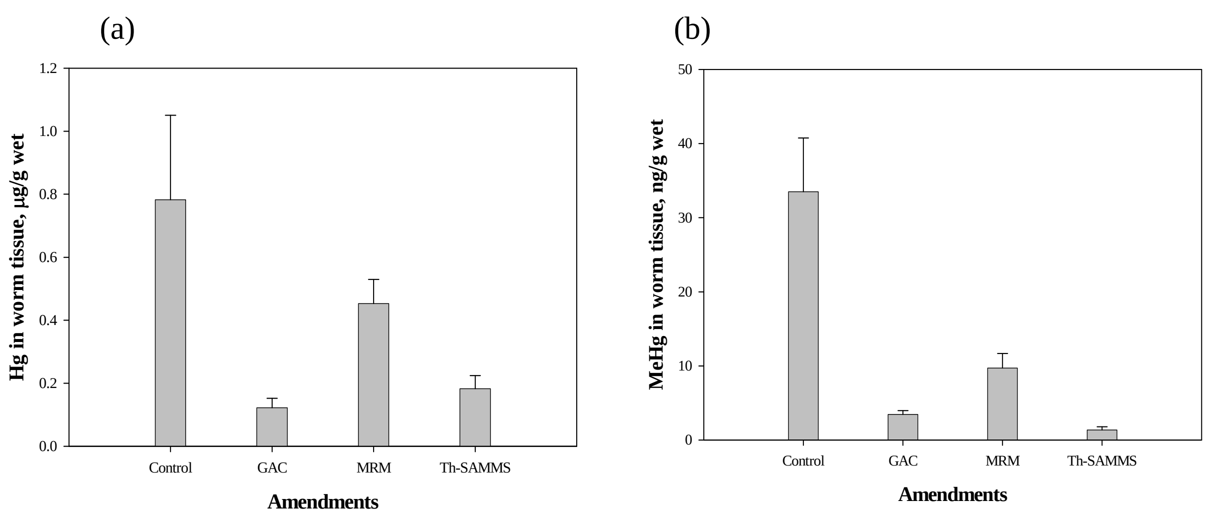


Figure 24. Concentration of total (a) and methyl (b) Hg in worm tissue after 14-day exposure of worms to River sediment.

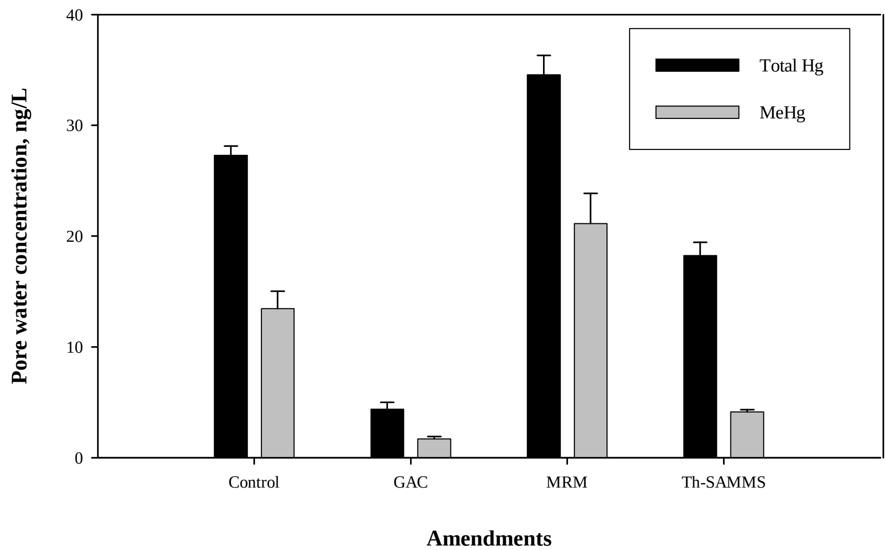


Figure 25. Concentration of total and methyl Hg in porewater after 14-day exposure of worms to River sediment.

VII. TECHNOLOGY TRANSITION EFFORTS

I) Leveraged funding and partnership with a small business

Technology transition efforts were significantly boosted through additional funding from an USEPA Small Business Innovative Research (SBIR) project and partnership with a small business (Menzie Cura and Associates [MCA]; Dr. C. A. Menzie and Mr. Ben Amos). The SBIR supported effort allowed collaboration of UMBC with MCA and significant progress towards transition of the technology and commercialization. A US patent application has been filed by UMBC and MCA based on the technology development. The agglomerate product has been named "SediMite™" and is being tested through pilot-scale demonstration studies.

We have made several presentations to groups of potential end users, vendors, and regulatory agencies. These presentations have helped us identify the most viable commercial applications listed below:

1. Application to sediments that pose low to moderate risk where alternatives other than dredging would be desirable;
2. Applications to sensitive environments where it is desirable to minimize habitat disruption (these include contaminated sediments located in aquatic or marine grass beds and wetland environments);
3. Application to hard to reach places (e.g., in and around pier structures)

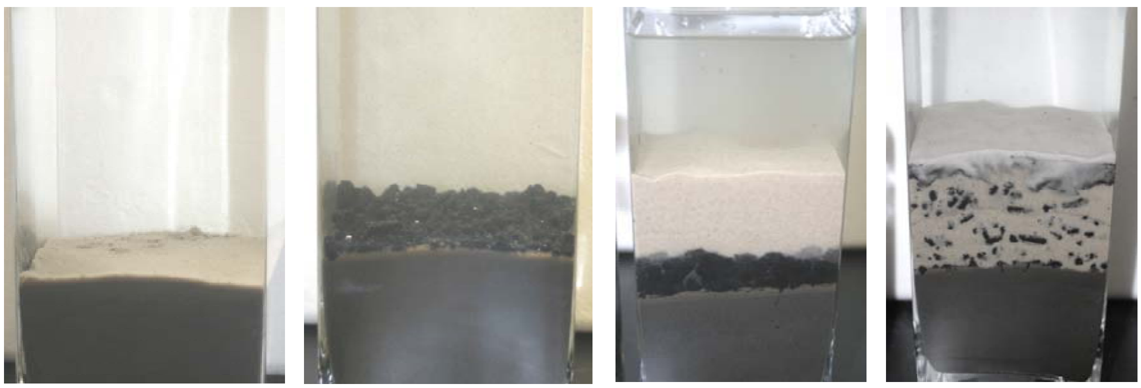
The application on sediments can be performed several ways and are illustrated in Figure 26.

1) <u>Application directly over the sediment surface</u> for eventual incorporation into the bioactive zone through natural mixing processes. This application would provide protection to the food chain by reducing contaminant bioavailability at the sediment surface and base of the food chain. Additionally, diffusive flux of contaminants from sediment into overlying water would be reduced. If ongoing sources are eliminated, and the area of application is a net depositional site, over time the amended sediment layer will be covered with a layer of clean freshly deposited sediments.

2) <u>Application as a layered active cap</u>. In this application the composite pellets would be placed as a layer on the sediment surface and covered with a layer of thin sand cap. This application may be appropriate for a site where contaminant upwelling with groundwater is a concern and providing a sand cover is needed to protect the carbon layer from hydrodynamic forces.

3) <u>Application as an amended sand cap</u>. In this application the composite pellets are mixed in with a sand cap during application thus distributing the amendments within the sand cap layer. Such an application would enhance the contaminant retardation capacity of the sand cap and reduce advective and diffusive transport of the contaminants from the sediment into the overlying water. This application would be appropriate for a site where hydrodynamic forces may cause the carbon to be mobilized unless stabilized with a sand cap.

The open water distribution device can be a barge-mounted dispersion device similar to a commercial fertilizer spreader as shown in Figure 27. The application device can include a large hopper and distributor mounted on the bow of a barge, which will be driven by an onboard drive device. The barge will also be motorized and include a navigation system. The barge will have to include storage space for one or more ton-bags of agglomerates. For example, RMT Inc. has adapted a sand-spreader for such an application illustrated in Figure 27 a. Another approach for dispersal of materials is to use one of the available technologies associated with application of thin-layer caps such as delivery near the sediment surface using a Tremie tube (Figure 27 b).



a) Sediment with no amendment or capping layer	b) sediment, with a layer of composite pellets covering the surface	c) sediment, with a layer of composite pellets and a layer of thin sand cap.	d) sediment, with a layer of amended sand cap where the pellets are mixed in the sand

Figure 26. Three different application modes of composite pellets.

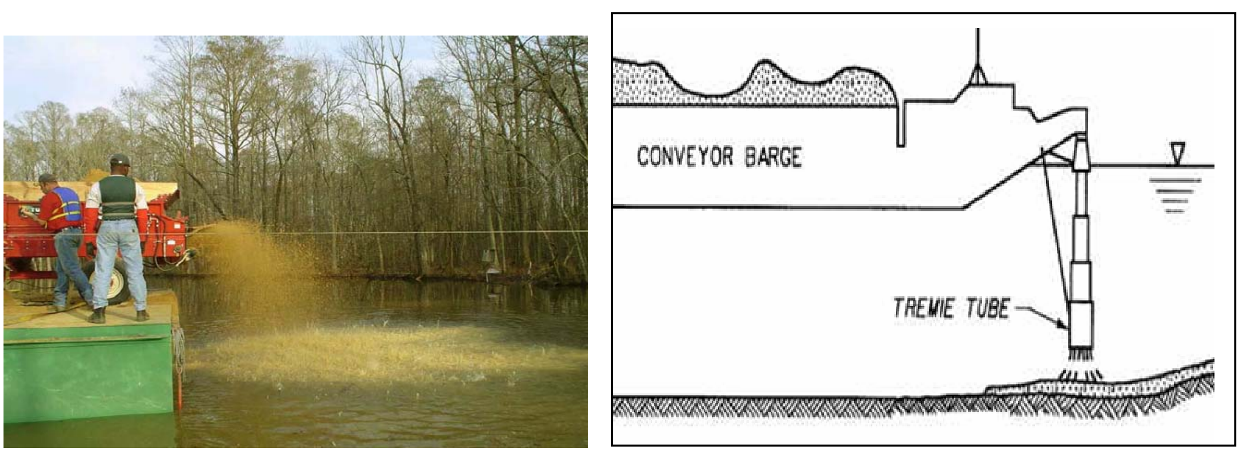


Figure 27. Potential methods for the application of composite pellets to sediments: a) picture on the left shows the use of a salt/fertilizer spreader device mounted on a barge, and b) picture on the right shows application near the sediment surface using a Tremie tube.

ii) Evaluation of manufacturing potential and cost of amendment composites.

Laboratory production of composite pellets was achieved using a manual extrusion device. In this research further effort was made to evaluate large-scale production of the pellets. Initial trial runs were performed at a pellet manufacturing facility named The Coating Place in Verona Wisconsin. Several batches of the pellets were produced at this facility in 2007 using large-scale equipment and tested in the laboratory. These initial trials helped assess the large-scale manufacturing feasibility. Subsequently, in 2008, hundreds of pounds of pellets were manufactured at a Pelleting facility in North Carolina. These trials at the Pelleting facility further evaluated the effect of different mix ratios on the product properties, tested the feasibility of production in large scale, and estimated production rates for the various formulations. Four different mixtures were processed through the pellet mill that will be used for industrial-scale production. These were extruded through a 5:1 die, which is the ratio of the width of the die (compression distance) to the hole diameter (larger ratio means more compression). The four trial batch runs at the production facility are summarized below:

Trial # 1 was a mixture of 60/30/10 PAC/Clay/Sand. The total weight was 50 lbs. of material, to which 20 lbs of water were added to bring the mixture to 37% moisture. It was found, however, that the sand and PAC contained moisture, and actual percent moisture in the mixture was 40.2%. Including the native percent moisture of the sand and clay, the actual ratio of dry masses was 55/33/12. This mixture did make pellets with a good consistency, but there were some problems with them sticking due to the excess moisture. If the moisture was a little lower, the formulation would produce great pellets. The pellets broke down within an hour in water and released thin clouds of carbon into the water when stirred.

Trial #2: Remaining portion of Trial #1 was re-mixed with more raw materials to obtain a true 60/30/10 PAC/Clay/Sand mixture at 35% moisture. The materials re-blended well, and extruded very nicely. It was noted that the pellets had a shiny surface, which indicates good compaction. The pellets produced in 36 seconds were collected and weighed and was used to calculate a production rate of 1550 lbs per hour. These pellets, although very good, could be further improved by either increasing the compression or increasing the moisture content 2%. These pellets were put in the air dryer and dried for an hour down to 8.2% moisture. The pellets sank in water with some release of trapped air, and also softened within an hour and released some carbon into the water when stirred. The release of carbon upon stirring can be minimized by using a larger particle size carbon in the mixture.

Trial #3: It was decided to find the upper-bounds of the sand content and a new mixture at 40/20/40 PAC/Clay/Sand was attempted with 37% moisture. Finer grain size sand was used. This mixture came out "like mud": it was very sticky. The actual moisture content was 37.55%. This mixture was not useable and was split into two portions: the first portion was set out to air dry to reduce moisture, and the rest used for Trial #4. The air-dried portion was able to make pellets that dropped in water after further drying to around 10% moisture.

Trial #4 was formed by adding sand and clay to Trial #3, which produced a mixture of 26/34/40 PAC/Clay/Sand. This mixture was run through the mill, and produced very sticky pellets. Reducing the moisture and rerunning the pelletization produced pellets that dropped through water well at about 10% moisture.

To summarize, the trial runs were successful in demonstrating the following:

1) It is possible to make the composite pellets at a large manufacturing facility to achieve production rates of 1550 lb/hr or 12,000 lb/8-hour shift. This is equivalent to an annual production capacity of about 3.5 million pounds at one production facility alone.

2) Moisture content of the final mixture is very critical in determining the physical consistency of the pelleting mixture ‘dough’. Native moisture content of the raw materials needs to be monitored carefully through the production process.

3) Each of the trials produced a pellet product that settled well through water and was useable. However, moisture content of the final mixture had to be adjusted.

4) Settling characteristics of the formed pellets were enhanced by allowing residual moisture content of about 10% in the final product. A slightly moist product wetted rapidly upon contact with water and sank readily. A fully dry product was slow in wetting.

5) Further fine tuning of the product formulation is ongoing to achieve optimal properties in the final mass-produced pellet.

<u>Estimated cost of production and application:</u> The cost listed below is rough estimates and may change with raw materials cost, and final cost of production in full-scale.

Cost of bulk AC is about $1/lb

Cost of sand and clay is less (assume 50% of AC)

Production cost is $2200/day of the Carolina facility that can produce about 7000 lb/d

Assuming 50% AC and rest sand and clay, cost of materials for 7000 lb of SediMite is $5250

Cost of production per day including materials= $7450

Management cost @ 10% = $745

Profit @ 20% = $1490

SediMite Licensing fee @ 6% = $447

Contingency @ 14%   = $1043

Estimated sale price = $11,175 for 7000 lb or $1.6/lb

<u>Estimated remediation cost using amendment pellets</u>. The above cost of amendment pellet production uses activated carbon as the sorbent material. In an ongoing pilot-scale study of sediment amendment in a river using activated carbon, the dose of carbon application was 5 lb/square yard. Estimating the same application rate of carbon per unit area, the dose of amendment pellets per acre is 50,000 lb. Using amendment pellet cost of $1.6/lb, this would result in a material cost of $80,000/acre. We anticipate pellet application using a barge mounted spreader device that would apply the material over the water column. In some engineering cost calculations performed for a full-scale application in Hunters Point and Grasse River, we were getting implementation costs in the same range as materials cost of amendment. So the total remediation cost may be about $160,000/acre, which is less than typical cost of dredging and disposal in a secure landfill. Further optimization of the delivery application can reduce the per acre treatment cost.

iii) Technology transition through ESTCP funded efforts

Two recently funded technology demonstration projects are evaluating the effectiveness of amendment pellets "SediMite™" in the field through ESTCP funding. These two projects are listed below:

1) ER-0835: Evaluating the Efficacy of a Low-Impact Delivery System for In-Situ Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals. (PI: Dr. C. A. Menzie). This project will perform technology demonstration of SediMite™ at two DoD site locations.

2) ER: 0825: In Situ Wetland Restoration Demonstration. (PI: Amy Hawkins). This project will evaluate SediMite™ technology along with a few other active capping technologies in side-by-side trials in the field at a DoD site.

iv) Partnerships with RPMs for testing of the technology at field sites

Significant effort was made towards teaming with practitioners to enable transition of the project accomplishments into technology demonstrations in the field. Several partnerships were developed with private industry and DoD site managers to take the technology forward into pilot-scale demonstrations. These efforts are listed below:

1) <u>Partnership with Rohm and Haas Company.</u>

A strong interest in the application and testing was expressed by Rohm and Haas Company (R&H) to evaluate the technology application at two of their impacted sites. One site is contaminated with DDT and the other one contaminated with Mercury. R&H has since provided financial and logistical support to evaluate the effectiveness of amendment pellets in reducing contaminant bioavailability in sediments from their two sites. These laboratory studies are ongoing and may lead to pilot-scale demonstrations at these sites if successful. The R&H company has also expressed interest in the licensing and production of the pellets if the technology is proven successful at field trials.

2) <u>Partnership with DuPont Company.</u>

The DuPont company has expressed interest in the application of the technology at two sites impacted with mercury and methyl mercury. Initial funding has been provided by DuPont to perform laboratory treatability studies using sediment samples obtained from these sites. Pilot-testing may follow at these sites if successful demonstration of methylmercury capture is achieved in the laboratory treatability studies.

3) <u>Partnership with Dow Chemical Company</u>

The Dow Chemical company has expressed interest in the SediMite™ technology in addressing dioxin contaminated floodplain soils and sediments. Recent work conducted at UMBC through support form Dow demonstrated the effectiveness of activated carbon in reducing the biouptake of dioxins by earthworms in floodplain soils.

4) Partnership at Ft. Eustis, Virginia.

The USUSEPA is overseeing the cleanup of Ft. Eustis which is on the National Priorities List. Interest in testing the SediMite™ technology was expressed both by the regulators and site project managers. In partnership with research collaborator Exponent, and site contractor, Malcolm Pirnie, a site survey and field sampling was conducted in the summer of 2008. Field sampling was performed at two locations in Bailey Creek on June 10 that had PCB concentrations in the range of 0.5 – 2 ppm based on historic sampling data. A treatability study was conducted at UMBC to evaluate the potential of using activated carbon as an amendment for in-situ remediation of PCB contaminated sediments at Bailey Creek in Ft. Eustis, VA. Current efforts are focused on planning for a pilot-scale demonstration of the technology at Bailey Creek and demonstrate reduction in PCB uptake in the food chain and associated risk reduction to humans. This effort is being supported through funding from the NIEHS Superfund Basic Research Program.

5) Partnership at Aberdeen Proving Ground, Maryland.

The two new ESTCP funded demonstration projects discussed earlier are being carried out at Canal Creek in Aberdeen Proving Grounds (APG). The regulatory community, site managers, and site contractors have expressed encouragement for the trial deployment of SediMite™ technology at several locations in APG. The chosen sites along Canal Creek are contaminated with mercury and PCB and provide a sensitive wetland type environment where the in-situ remediation would be most appropriate. Treatability studies using sediments from these sites are ongoing and pilot demonstrations are being planned in the summer of 2009.

v) Survey of other DoD facilities that could benefit from the technology

A survey of DOD facilities that could potentially benefit from this technology was performed using publically available reports found in the following databases: USUSEPA Superfund, USACE Center for contaminated sediments, General Electric's Contaminated Sites and Defense Base Closure and Realignment Commission. This survey focused on sites that have PCB and metals co-located at contaminated sediment areas. An initial list of 134 contaminated sediment sites were obtained and narrowed down to 13 based on comprehensive information regarding the contaminants of concern (COC), sediment characterization data, remedy and remedy effectiveness (Table 9). Dredging and disposal was the chosen remedy for approximately 70% of the sites while the remaining sites employed enhanced natural recovery, monitoring and/or capping. Approximately 85% of these contaminated sites had metals and PCB co-located in sediment. Davisville Naval Construction Battalion Center/OU1 Site 9 (Davisville), Eielson Air Force Base/OU7 (Eielson) and Puget Sound Naval Shipyard Complex/OU2 (Puget Sound) did not achieve remedial action objectives. The chosen remedy for these sites primarily consisted of dredging, confined disposal, enhanced natural recovery and long-term monitoring. PCB are COC at these sites and at Davisville and Pugent Sound, PCB are co-located with metals and PAH. Therefore, a multi-functional sorbent amendment cap may be appropriate at these sites. Further evaluation of the remaining 131 sites is necessary to identify potential candidates for in-situ remediation with a multi-functional sorbent amendment cap.

Table 9. List of DoD facilities with PCB and mercury in sediments that could directly benefit from this research

	DOD Site/OU[1]	Location	Water Body	Contaminant	Characterization Data[1]		RI/FS Stage[2]	Remedy[1,2,3]	RAO[1]		Remedy Effectiveness[3]	BRAC[4]
					Concentration (mg/kg)	Vol, Depth			Quantity (mg/kg)	Quality		
1	Davisville Naval Construction Battalian Center/OU1 Site 9	North Kingston, RI	Allen Harbor	Metals, PAH, PCBs	Max Concentrations:PAH 75; cPAH 44; SVOCs 81; Metals 369,000;		Long-term Monitoring	1) Removal and covering of landfill debris from the site shoreline, 2) Construction of a stone revetment along the shoreline to protect the landfill from wave action, 3) Construction of a breakwater structure along with a wetland area between the revetment wall and breakwater structure 4) Long-term monitoring of sediment and shellfish contaminant concentrations	PCBs 1;	1) Minimize risks from marine ecological exposure to COC in sediment, 2) Control potential future sediment contamination from landfill constituents, 3) Control potential future contamination of shellfish from landfill constituents, 4) Prevent or minimize human ingestion of shellfish from the landfill shoreline containing COC above health advisory concentrations.	PCB and PAH in sediment were detected in the vicinity of the soil removal action of Spring 1999. (2006)	X
2	Naval Surface Warfare Center/OU3, OU4, OU5, OU7, OU16	Dahlgren, VA	Gambo Creek	VOCs, SVOCs, Metals, Pesticides, PCBs, Inorganics	OU3 VOCs 0.005-0.58; SVOCs 0.025-1; Pesticides 0.0034-9.1; Cu 5,390; Pb 743; OU4 Hg 0.01-0.125; OU5 Hg 0.66; PCB 0.0058; OU7 SVOCs 0.046-2.3; Metals 0.21-37,400; TOC 10,400-31,700; VOCs 0.01-7.2; OU16 TAL Metals 0.2-94,400; 4,4'-DDD 0.57; 4,4'-DDE 0.13; 4,4'-DDT 0.073; TPH 10.4-55.9;	OU5- Vol 970 cy	OU3, OU5-Remedy Construction Complete, OU4, OU7, OU16-Remedy Study/Selection Complete	OU3-1) Cap, 2) Shoreline protection, 3) Institutional controls and 4) Monitoring. OU4-1) Fish catch and-release and monitoring programs to determine when the fish tissue concentrations decrease to acceptable levels, 2) Institutional controls to prevent fish consumption. OU5- 1) Excavate 2) Offsite TDF, 3) Institutional controls and 4) Longterm monitoring. OU7, OU16- No action for sediment, surface water, and fish tissue.		1) Eliminate threat to human and ecological receptors. 2) Confirm sediment concentrations are not increasing in biologically active zone.	Remedy functioning as intended. (2005)	
3	Eielson Air Force Base/OU7,	Fairbanks, AK	Garrison Slough Creek	PCBs	PCBs -ND-55;	Area 984 ft; Vol-730 cy; Depth 3.3 ft;	Remedy Construction Complete	1) Fishing restrictions, 2) Fish Barriers, 3) Excavation of PCB concentration > 10; 4) Onsite disposal when PCB concentration>10 and Offsite when >50, 5) Institutional and Engineering Controls and 6) Long-termMonitoring.	Remove PCBs >10; Fish tissue PCBs 0.69;	1) Prevent fish ingestion 2) Reduce mass of PCBs bioavailable	Remedy did not reduce PCB levels in fish tissue to RAO. (2004)	X
4	Bangor Naval Submarine Base/OU6 Site 26	Silverdale WA	Hood Canal	PAHs, Metals, Phthalates, Phenols, and Chlorinated Pesticides	SVOCs 0.009-2.4; Organics 2.2-3,1700; (ppm-OC) Metals 0.02-1,900; (ppm-dw)	Depth 0-6 ft;	Long-term Monitoring	Sediment and Clam Tissue Monitoring to ensure concentrations are not increasing in biologically active zone.		Ensure concentrations are not increasing	Remedy protective based on recreational exposure to clams and sediments. (2005)	X
5	Air Force Plant #4	Fort Worth, TX	Meandering Rd Creek to Lake Worth	VOCs, SVOCs, PCBs, Metals	Meandering Rd Creek As 3.1-6.1; Cd ND-2.4; Cu 13.4-17.8; Pb 10-77.4; Ag ND-6.9; Zn 17.8-87; Lake Worth:As 3.5-6; Cd(0.4-11.4; Cu 8.5- 88.4; Pb 8-444; Ag ND-13; Zn 21.9-303; VOCs 1; SVOCs 1.3-7.9; PCB 0.1-0.11;		Long-term Monitoring	No Action and Monitoring	Ag 1.0; and PCB 0.1;	Prevent ecological exposure through monitoring	Remedy functioning as intended (2004)	X
6	Newport Naval Education & Training Center/OU4	Newport, RI	Naragansett Bay	PCBs, PAH, Metals		Vol 34,000 cy	Long-term Monitoring	1) Dredging, 2) Screening by Size (for reuse), 3) Dewatering, 4) Treatment/Discharge dewater liquids, 5) Disposal offsite, 6) Backfilling, 7) Habitat Restoration and 8) Monitoring.	Pore water Cu 0.053; Ni 0.033; Sediment Anthracene 0.5; Fluorene 0.2; Pyrene 3; PCBs 3.6;	1) Prevent fish ingestion 2) Prevent birds and fish from contaminated sediment exposure 3) Minimize migration contaminated sediment and landfill washout to marine environment.	Remedy effective (2005)	X
7	Marine Corps Combat Development Command/OU4	Quantico, VA	Potomoc River	PCBs, PAHs, Pesticides, Metals	SVOCs 13-1267; Pesticides 2.7-1606; PCBs 25-2280; Metals 0.27-16670;		Long-term Monitoring	1) Excavation and off-site disposal of swale sediment w/PCBs >10; 2) Excavation and onsite disposal of landfill and sediment material from shoreline, 3) Shoreline stabilization, 4) Wetland mitigation and 5) Institutional Controls.	Excavate PCBs >10	1) Minimize direct contact, inhalation, and ingestion of contaminants posing a carcinogenic risk. 2) Restrict migration of contaminants to the adjacent embayment	Remedy effective (2003)	
8	Puget Sound Naval Shipyard Complex/OU2 (or OU B)	Bremerton, WA	Puget Sound	PCBs, PAHs, Metals	PCBs 1.57-61.7 of OC; HPAH 0.27-4,640 of OC; LPAH 0.63-998 of OC; As 2.3-111; Cu 5.4-1,700; Pb 2.7-1,500; Zn 23.9-7,390; TOC 0.5-7.9%;	Vol 200,000 cy; Depth 0-10 cm;	Remedy Construction Complete. (Must address contamination CAD to be complete.)	1) Enhanced Natural Recovery, 2) Dredging (to min of 2 ft), 3) Confined aquatic disposal (CAD) for dredged sediment, 4) Thin-layer sediment layer in-situ cap 5) Habitat restoration, 6) Shoreline stabilization and 7) Long-term Monitoring and Maintenance.	Sediments: reduce concentration to <3 OC PCB in biologically active zone; Dredge/Dispose/CAP >6 PCB and >3 Hg; Enhanced Natural Recovery >9 PCB;	1) Reduce PCBs in the biologically active zone (0-to 10-cm depth) to <3 ppm OC to reduce PCB concentrations in fish tissue 2) Control shoreline erosion of contaminated fill material 3) Selectively remove sediment with high concentrations of mercury colocated with PCBs	Contamination Found near confined aquatic disposal pit. (2002)	X
9	Alameda Naval Station/OU9 Site 17	Alameda, CA	San Francisco Bay	Metals, PCBs, Metals, Pesticides, Butyltin Compounds, Radionucleoides	Metals 1.5-514; PCBs 18-2535; DDx 2.4-202; HPAH 18-36380; LPAH 88-6768; Pesticides 0.1-28; Butyltin Compounds 2-185;	Depth 0.3-5 ft; vol 63,000 cy;	Study and Remedy Selection Underway	1) Dredge to 4 ft plus 1 ft overdredge allowance., 2) Dewater on-site in temporary drying beds and 3) Upland Disposal at a Permitted Off-Site Waste Disposal Facility.	Cd 24.4; PCBs 1.13; DDx 0.13;	1) Protect fish-eating birds from exposure to PCBs, DDx, Pb and Cr, 2) Protect fish from exposure to Cd in sediments, 3) Reduce potential biomagnification of PCBs		X
10	Loring AFB/OU 13	Limestone, ME	Greenlaw Brook (to Malabeam Lake), Wolverton Brook/Brandy Brook (to Little madawaska River), Butterfield Brook/Limestone Stream (Aroostock River ultimately)	PCBs, PAHs, DDT, Chlordane, Metals	Max Concentrations: PAH 270; Pb 454; Zn 952; PCB 6.4;	Vol 93,000-152,328 cy; Depth 2 ft;	Long-term Monitoring	1) Dredging, 2) Dewatering, 3) Disposal in CDF, 4) Confirmation sampling and 5) Fish advisory.	PAH 35; Pb 218; Zn 410; PCB 1; DDT/DDD/DDE 0.28; Chlordanes 0.48; Fish tissue: 4.4'-DDD 0.6; 4,4'-DDE 1.09; 4,4'-DDT 0.04; PCB 0.031;	1) Prevent/minimize ingestion of and dermal contact with contaminated sediment by human and ecological receptors, 2) Prevent human ingestion of contaminated fish, 3) Minimize migration of contaminated sediment, and 4) Avoid destruction of existing ecological habitat where the risk associated with short-term habitat loss outweighs the reduction in risk potentially realized by site remediation.	Remedy effective (2005)	X
11	Norfolk Naval Shipyard/OU2 Site 2	Norfolk, VA	Drainage Channel to Mason Creek (Willoughby Bay ulitimately)	Metals, Pesticides	4,4'-DDE 2.8-31; 4,4'-DDD 22-140; As 0.93-25.3; Cd 2.5-48.1; Cr 33.7-292; Cu 117-5,510; Pb 129-3,900; Ni 26.5-62.7; Ag 168-1,040; Zn 539-1,900; Fe 2,160-49,500;	Vol 1,000 cy; Depth 2 ft;	Long-term Monitoring	1) Dredging, 2) Dewatering, 3) Disposal off-site, 4) Bank stabilization and 5) Monitoring. If RAO not met, capping and backfilling will be implemented.	Pb 218;	Prevent adverse ecological effects	Remedy Effective (2003)	X
12	New London Submarine Base/OU3	New London, CT	Thames River	Metals, Pesticides	4,4'-DDD 0.059-850; 4,4'-DDE 0.017-15; DDT 0.025-94; Dieldrin 0.014-0.86; As 0.58-39.9; Pb 4-661; Cd 1.1-30.1; Mn 52.9-2,850; Zn 6.3-2,720; TOC 83-53,000;	Vol 6,800 cy; Depth 2.3 ft;	Long-term monitoring	1) Dredging, 2) Onsite Dewatering, 3) Offsite disposal, 4) Wetlands/Waterway restoration and 5) Monitoring.	DDTR 2; Dieldrin 0.195; Cd 9.6; Pb 218; Zn 410;	1) No human ingestion >DDT 27, DDD 38, Dieldrin 0.57, As 6.1, Be 2.1; Not to enter food chain >DDTR 2, Dieldrin 0.045, Cd 9.6, Pb 218, Zn 410 (ER-M values)	Remedy effective (2006)	X
13	Yorktown Naval Weapons/OU2 Site 6, OU3 Site 9	Yorktown, VA	Felgrates Creek (York River ultimately)	Metals, SVOCs, Nitramines	OU2 SVOCs 0.17-2.4; Inorganics 0.33-27,000; VOCs 0.008-190; Nitramines 0.21-2,500; Inorganics 0.73-38,900; OU3 Inorganics (As, Be, Cr) 0.26-55.5; SVOCs 42 2600; Nitramines 120-3700	OU2 Vol 1,000 cy; Depth 4'	Long-term monitoring	OU2 1) Excavation sediments, 2) On-site staging and treatment area for ex-situ bioremediation, 3) Offsite disposal, 4) Habitat restoration and 5) Long-term monitoring. OU3 No Action	OU2 TCE 16; Total cPAHs 10; Total Amino-DNTs 10; HMX 5.7; RDX 5; 1,3,5-TNB 1.6; 2,4,6-TNT 14; Ni 52; Zn 410;	OU2 Mitigate exposure of contaminated sediments to potential human and ecological receptors	OU2 Remedy effective (2002)	X

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Abbreviations: 0.692307692

COC-Contaminant of Concern; cPAH- carcinogenic polycyclic aromatic hydrocarbon; PAH-polycyclic aromatic hydrocarbon; PCB- polychlorinated biphenyl; 0.846153846

RAO- Remedial Action Objective; ND- Non Detect; ERM - Ecological Range Median; cy - cubic yards; ft - feet; USEPA- U.S. Environmental Protection Agency;

USACE- United States Army Core of Engineers; RI/FS- Remedial Investigation/Feasibility Study; SVOC- Semi-volatile organic compounds; VOC- Volatile organic compunds;

DDD- dichlorodiphenyldichloroethane; DDE- dichlorodiphenyldichloroethylene; DDT- dichlorodiphenyltrichloroethane; TNB- 1,3,5-Trinitrobenzene; TNT- 2,4,6-trinitrotoluene;

VIII. CONCLUSIONS AND FUTURE WORK

The main conclusions of this research project are:

1) Sorbent amendments are available that can reduce the bioavailability of hydrophobic organics such as PCB and heavy metals present in sediments. Several of these amendments were tested in this research and demonstrated to be effective in reducing porewater concentration and benthic organism bioaccumulation of metals and organics in contaminated sediments.

2) Various sorbent amendments can be delivered to sediments via a common platform of composite pellets that sink through the water column readily and slowly release the sorbent ingredients at the sediment surface.

3) The tested sorbent amendments for metals and organics (e.g. activated carbon and Thiol-SAMMS) did not negatively impact the performance of each other when applied together.

4) Sorbents delivered in the agglomerated form reduced contaminant bioavailability in sediments as effectively as the same sorbents added directly to sediments without mechanical mixing.

5) The chosen sorbent amendments demonstrated little or no toxicity to two freshwater and two marine benthic organisms that were tested.

6) Agglomerate pellets production can be scaled up to full-scale using formulations developed in this research.

7) This research successfully demonstrated the reduction of biouptake of mercury and methylmercury from sediments after amending with two sorbents: activated carbon and Thiol-SAMMS.

8) The technology is ready for testing at pilot-scale demonstration projects in freshwater and estuarine environments.

Additional effort in the future is needed in the following areas:

1) Pilot-scale testing at sites offering different sediment types, hydrodynamic environments, benthic organism diversity, and contaminant type. These studies need to test the application under realistic conditions and determine conditions where the technology may be successful.

2) Further effort is needed to develop new sorbent materials that are designed for application to sediment contaminants. In the present work we tested engineered sorbent materials that were developed for water treatment applications. For example, new products developed through advances in material science that can incorporate metal sorption in a matrix such as activated carbon will be very promising.

3) Additional work is needed to evaluate different modes of application of sorbent amendment pellets to sediments including incorporation into an active sediment cap.

4) Pilot-scale effort is necessary in collaboration with companies involved with sediment management to develop new equipment for the cost-effective delivery of amendment pellets on the sediment surface to achieve a uniform spatial distribution while keeping sediment/amendment resuspension to a minimum.

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IX. APPENDICES

APPENDIX I

Technical Paper 1

Evaluation of Sorbent Amendments for In Situ Remediation of Metal Contaminated Sediments.

Seokjoon Kwon, Jeffrey Thomas, Brian E. Reed, Laura Levine, Victor S. Magar, and Upal Ghosh

Technical Paper 2

Development and Testing of a Low-Impact Delivery System for Sediment Amendments.

Jeffrey Thomas, Upal Ghosh, Ben Amos, and Charles Menzie

Technical Paper 3

Bioavailability Reduction of Mercury, Methylmercury, and PCBs in Sediments Using Multifunctional Amendments.

Seokjoon Kwon, Brian E. Reed, and Upal Ghosh

APPENDIX II

ABSTRACTS OF PAPERS AND POSTERS PRESENTED AT CONFERENCES:

Presentation:
New advances in sediment remediation: Reducing Contaminant Bioavailability. Upal Ghosh. ERM'S PROBLEM SITE SERIES CONTAMINATED SEDIMENT STRATEGIES, October 30, 2008 – Princeton, New Jersey

Presentation:
Sorbent amendments to reduce mercury bioaccumulation in sediments. Upal Ghosh, Workshop on New Advances in Sediment Remediation. November 14, 2008, 8:00 am—12:30 pm Technology Research Center, Room 206, UMBC.

Presentation:
In-situ Remediation Update: PCB Bioavailability Reduction in Sediments Using Activated Carbon Amendment, Upal Ghosh. Sediment Management Workgroup Meeting, New Orleans, January, 2008.

Poster:
Development of Multifunctional Amendment Mixtures and Composites for In Situ Remediation of Contaminated Sediments. Seokjoon Kwon, Jeff Thomas,Upal Ghosh, Brian E. Reed, Victor Magar, Todd Bridges, Cynthia Gilmour. SERDP Bioavailability Workshop. 2008.

Presentation:
Combining Engineering and Biology in a low-impact In-Situ Treatment System for Sediments Charles A. Menzie, Ben A. Amos, Upal Ghosh, Jeffrey Thomas. SETAC NA Meeting, Nov, 2008.

Posters at SERDP Annual Symposiums: 2006, 2007, and 2008:
Rational Selection of Tailored Amendment Mixtures and Composites for In Situ Remediation of Contaminated Sediments (ER-1491). Upal Ghosh, Brian E. Reed, Seokjoon Kwon, Jeff Thomas, Victor Magar, Todd Bridges, and Daniel Farrar.

Presentation:
Combining Engineering and Biology in a Low-Impact In-Situ Treatment and Capping for Sediments: applications to sites contaminated with PAHs, PCBs, and mercury. C.A. Menzie. Parsons Biweekly Webinar Series, Jan 14, 2009.

Presentation:
In-situ reduction of contaminant bioavailability in sediments. U. Ghosh. EPA Region II BTAG Meeting, New York, NY. May 23, 2007.

Presentation:

Remediation of Contaminated Sediments: Current Challenges and Emerging Technologies. U. Ghosh. Center for Environmental Science and Engineering, Indian Institute of Technology, Bombay, India. July 29, 2008.

Presentation:
In-situ PCB Bioavailability Reduction in Sediments: Fundamental Laboratory Investigations to Field Studies. Seminar, University of New Hampshire, Dept of Civil and Environmental Engineering. Oct 6, 2006.